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Inorganic Contaminant Accumulation in Potable Water Distribution Systems

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Background and Disclaimer

The USEPA is revising the Total Coliform Rule (TCR) and is considering new possible distribution system requirements as part of these revisions. As part of this process, the USEPA is publishing a series of issue papers to present available information on topics relevant to possible TCR revisions. This paper was developed as part of that effort.

The objectives of the issue papers are to review the available data, information and research regarding the potential public health risks associated with the distribution system issues, and where relevant identify areas in which additional research may be warranted. The issue papers will serve as background material for EPA, expert and stakeholder discussions. The papers only present available information and do not represent Agency policy. Some of the papers were prepared by parties outside of EPA; EPA does not endorse those papers, but is providing them for information and review.

Additional Information

The paper is available at the TCR web site at:

http://www.epa.gov/safewater/disinfection/tcr/index.html

Questions or comments regarding this paper may be directed to **TCR@epa.gov.**

INORGANIC CONTAMINANT ACCUMULATION IN POTABLE WATER DISTRIBUTION SYSTEMS

December 2006

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1.0 Introduction

The M/DBP Federal Advisory Committee concluded that EPA should review and evaluate available data and research on those aspects of distribution systems that may create or pose risks to public health as a part of the Six-Year Review of the Total Coliform Rule. These conclusions and those of the Six-Year Review process are discussed further in "Total Coliform Rule and Distribution System Issue Papers Overview." The current TCR requires utilities to take total coliform samples in the distribution system, and this monitoring constitutes the majority of distribution system monitoring. While this monitoring may capture and identify several microbial contamination event pathways in the distribution system, it was not designed to capture the range of risks that were identified by the M/DBP Federal Advisory Committee.

EPA plans to assess the effectiveness of the current TCR and determine what alternative and/or additional risk reduction strategies are available, and to consider revisions to the TCR with new requirements for ensuring the integrity of the distribution system. To help achieve these goals, it is important to understand 1) distribution system contamination mechanisms and pathways, 2) how water quality conditions can impact public health, and 3) tools available for, and issues related to, identifying and assessing potential distribution system public health risks.

As the understanding of these contaminants and pathways increase, an increased awareness of the potential public health risks posed by distribution systems is obtained. The following quote summarizes this in respect to inorganic contaminant accumulation.

> *Historically, it has been thought that inorganic contaminants (other than lead, iron, and copper) maintain essentially constant concentrations as water passes through the water distribution system; this behavior would be termed conservative in the chemistry sense. Consequently, regulatory monitoring of inorganics has been required only at entry points to the distribution system, presuming that the concentrations cannot increase and that such monitoring is sufficiently protective of public health. In addition, the concentrations of most inorganic contaminants have been considered sufficiently constant at these locations to allow intermittent monitoring without jeopardizing consumer protection. However, a detailed examination of these assumptions reveals a body of considerable research that casts doubt on any presumption of conservative behavior by many potential inorganic contaminants. Even now, some consumers may unwittingly be exposed to undesirable concentrations of inorganic contaminants that are not part of the current monitoring framework. (Schock, 2005)*

Consumers do not drink water directly from the source or immediately after treatment; rather, they drink water that has traveled from the source to their taps via distribution system pipes. Therefore, consumers drink water that may have changed in quality during its time in the distribution system. This paper discusses:

- the accumulation of inorganic contaminants of potential concern in distribution system scales, sediments, and biofilm,
- factors that may lead to contaminant accumulation and subsequent release back into the drinking water,
- monitoring methods to determine contaminant accumulation,
- methods for potentially controlling contaminant accumulation and release,
- case study examples, and
- areas for additional research.

Because currently required monitoring data do not necessarily reflect the water quality in the distribution system or that delivered to the consumer, the amount of published literature specific to contaminant concentrations within distribution systems is relatively small. The objective of this paper is to characterize the potential for accumulation and release of inorganic contaminants, based on available published literature.

Within the context of this paper, a distribution system is defined as a system of conveyances that distributes potable water. All pipes, storage tanks, pipe laterals, and appurtenances that comprise the delivery system are included in this definition. Appurtenances owned and operated by private customers, such as service lines and plumbing components, that are typically not considered the responsibility of the public water system purveyor are also considered in this definition because they are physically attached to the distribution system and could potentially be a source of contamination, through, for example, backflow or leaching of contaminants from service lines. These and similar events may affect the water quality under the purveyor's jurisdiction. However this paper does not consider indicators that specifically identify problems in household plumbing.

2.0 Contaminant Transport

Contaminants may enter the distribution system through a variety of mechanisms including:

- in a dissolved state in the source water,
- attached to turbidity particles in the source water,
- added to the source water from treatment chemicals,
- as by-products of corrosion of piping and plumbing materials, or
- through cross-connections or other breaches in the distribution system.

Under certain conditions, contaminants such as nitrate, nitrite, or radon may form within the distribution system.

The fate and transport of contaminants, and their subsequent accumulation and release within the distribution system, regardless of the mechanism of entry, is a complex process controlled by a number of chemical, physical, and microbial mechanisms. Figure 2-1 provides a conceptual overview of the distribution pipe network as a contaminant reservoir and the potential transport pathways that are discussed in this paper.

Most surface water is filtered to reduce the turbidity below the regulatory limit of 0.3 NTU for conventional or direct filtration and 1 NTU for all other treatment technologies, although most surface water systems will operate at levels less than 0.1 NTU to ensure they are well under the regulatory limit of 0.3 NTU. As the turbidity is reduced, the inorganic contaminants that are carried in by the turbidity particles are likewise reduced. However, the turbidity in most (unfiltered) ground water supplies is not reduced and the contaminants attached to the turbidity particles enter the distribution system wholesale. Ground water turbidity levels between different systems may vary from 0.1 to 1.2 NTU, which relates to the potential inorganic contaminant loading rate to the distribution system. Whether from a surface water source or a ground water source, unless the turbidity is zero, it is possible that some accumulation of inorganic contaminants will occur. Thus, even at the regulatory limit of 0.3 NTU for surface water supplies, it is possible for inorganics to be introduced to, and accumulate within, the distribution system. Furthermore, reductions in source water turbidity do not necessarily remove dissolved constituents that may have been added during the treatment process, such as aluminum, calcium, iron, or fluoride.

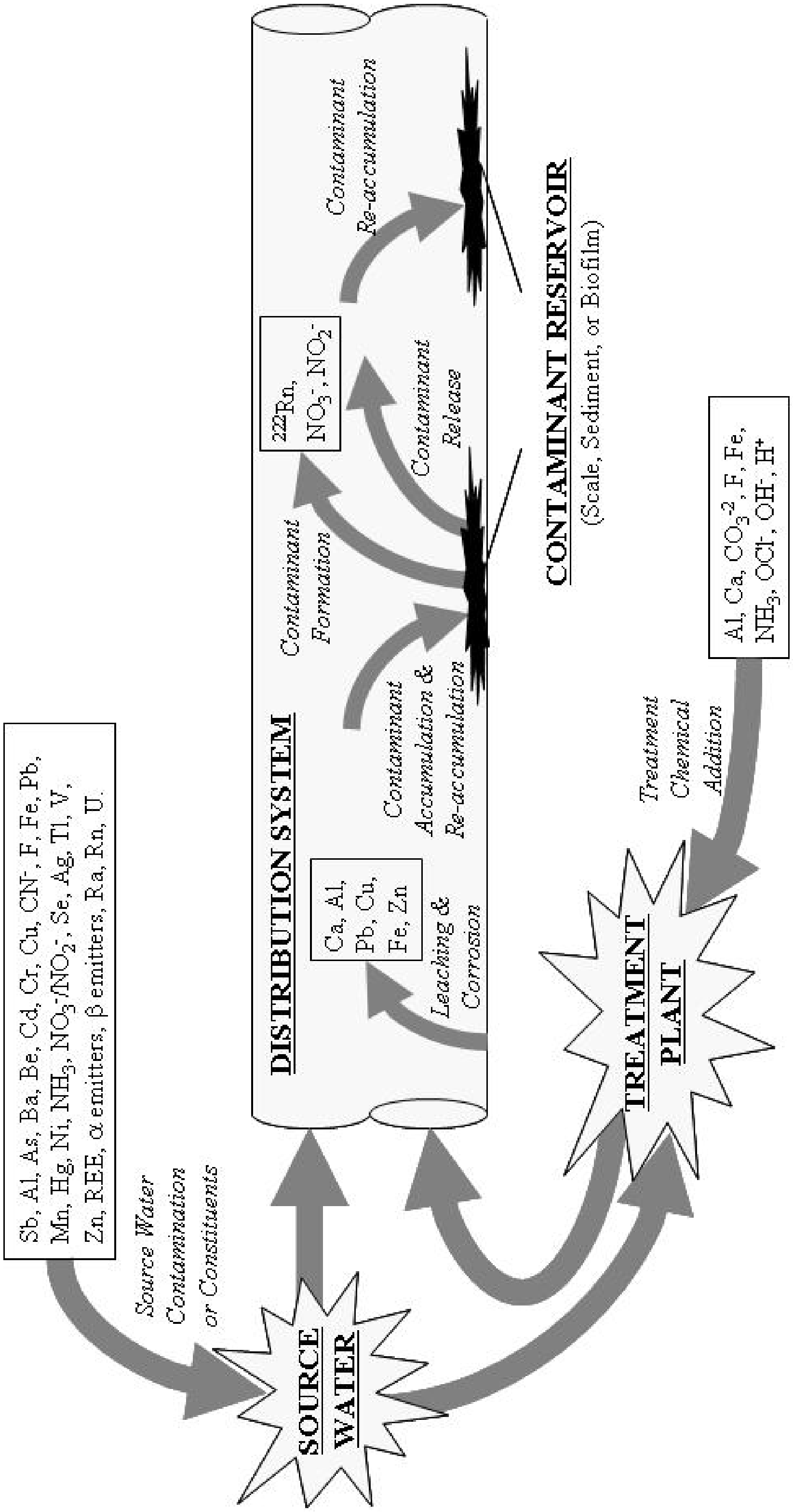

Figure 2-1. Conceptual Overview of Inorganic Contaminant Transport Pathways and Reservoirs.

3.0 Regulated Contaminants and Contaminants of Potential Concern

As part of the National Primary Drinking Water Regulations, the USEPA has developed primary drinking water standards for 16 inorganic compounds and four radiological compounds. With the exception of lead and copper, these compounds are regulated with primary Maximum Contaminant Levels (MCLs). The primary MCLs were developed based on consideration of potential chronic health effects associated with long-term consumptive exposure to low levels of these compounds. Since fate and transport of inorganic and radiological compounds was assumed to be conservative during development of these standards, compliance with the MCLs is based on the running annual average of quarterly results at the entry points to the distribution system. Lead and copper are regulated with action levels that apply at customer taps within the distribution system.

As part of the National Secondary Drinking Water Regulations, the USEPA has also developed secondary drinking water standards for 15 inorganic and physical parameters. These parameters are typically associated with aesthetic properties of water, such as color or taste. However, some secondary parameters (e.g., iron, manganese, aluminum) may also serve as distribution system accumulation reservoirs for primary compounds. The secondary MCLs are unregulated at the federal level, although individual state agencies may adopt enforceable standards.

While the existing primary MCLs may be protective based on long-term exposure, they may not adequately address periodic and transient water quality changes that can occur in the distribution system due to contaminant accumulation and release. These phenomena have the potential to produce elevated concentrations of primary compounds at customer taps on a daily, seasonal, or even longer-term basis. Depending on the magnitude, duration, and frequency of contaminant release, the potential for acute and/or sub-chronic health effects may exist due to consumptive exposure. At present, drinking water standards intended to safeguard against acute and/or sub-chronic conditions generally do not exist, with the exceptions being the nitrite/nitrate MCLs and action level for lead.

Tables 3-1, 3-2, and 3-3 provide an overview of the regulated inorganic compounds, unregulated inorganic compounds, and regulated radiological contaminants, respectively. These tables provide information on the following, where applicable and available: contaminant MCLs and Maximum Contaminant Level Goals (MCLGs); chronic oral intake reference dose; slope factor for carcinogens; potential chronic health effects; Health Advisory Levels (HALs) as reported by USEPA (1995b); other reported contaminant levels that may lead to acute or sub-chronic health effects; and potential acute and sub-chronic health effects. Additional information and discussion on health effects associated with each contaminant can be found in Appendix A.

Table 3-1. Regulated Inorganic Contaminants

Contaminant	MCL & MCLG [A]	Chronic Oral RfD [B] and/or SF [C]	Potential Chronic Health Effects from Consumption Above the MCL [D]	HAL[E] 1-10d (≤ 7y)	Other Reported Acute/Sub-Chronic Doses	Potential Acute and Sub-Chronic Health Effects from Consumption Above the HAL [D]
Antimony (Sb)	0.006 mg/L	RfD: $4x10^{-4}$ mg/kg/d	Decreased longevity, altered blood levels of glucose and cholesterol. [F,G]	0.01 mg/L (0.01 mg/L)	0.53 mg/kg [F]	Nausea, vomiting, diarrhea, respiratory difficulties. [F,G]
Arsenic (As)	0.010 mg/L	RfD: $3x10^{-4}$ mg/kg/d SF: 1.5 $(mg/kg/d)^{-1}$	Skin damage or problems with circulatory system. Possible increased risk of cancer. [H]	NA	20 µg/kg/d [H]	Nausea, loss of appetite, vomiting, epigastric and abdominal pain, diarrhea. [H]
Barium (Ba)	2 mg/L	RfD: 0.07 mg/kg/d	Hypertension. [G,I]	None	0.8 g (lethal) [I]	Gastrointestinal disturbances (vomiting, diarrhea), muscular weakness, elevated blood pressure. [G,I]
Beryllium (Be)	0.004 mg/L	RfD: 0.002 g/kg/d	Damage to bones and lungs. Possible increased risk of cancer [G,J]	30 mg/L (4 mg/L)	None	None known. [G,J]
Cadmium (Cd)	0.005 mg/L	RfD: $5x10^{-4}$ mg/kg/d (water)	Renal toxicity kidney damage (renal dysfunction, hypertension, anemia). [G,K]	0.04 mg/L (0.005 mg/L)	20 mg/kg (lethal) [K]	Nausea, vomiting, diarrhea, muscle cramps, salivation, sensory disturbances, liver injury, convulsion, shock, and renal failure. [G,K]
Chromium (Cr)	0.1 mg/L	RfD: 0.005 mg/ kg/d as Cr(VI)	Damage to liver, kidney circulation, and nerve tissue, and dermatitis. [G,L]	1 mg/L	71 mg/kg (lethal) [L]	Skin irritation or ulceration. [G,L]
Copper (Cu)	1.3 mg/L [M] 1.3 mg/L (MCLG) 1.0 mg/L (SMCL)	RfD: 0.005 mg/kg/d as CuCN	Kidney, liver, and nervous system damage. [G,N]	None	2.2 mg/l [N]	Stomach and intestinal distress, liver and kidney damage, and anemia. [G,N]

[A] USEPA, 2003. The Maximum Contaminant Level (MCL) and the Maximum Contaminant Level Goal (MCLG) are identical unless stated otherwise. Secondary Maximum Contaminant Level (SMCL) is given if applicable.

[B] RfD: Chronic oral reference dose for non-carcinogenic toxic health effects based on findings of No Observable Adverse Effect Level (NOAEL) or Lowest Observable Adverse Effect Level (LOAEL).

[C] SF: Slope factor is the upper-bound incremental risk of developing cancer due to lifetime exposure to a particular unit intake.

[D] Chronic refers to the health effects due to long term exposure to the contaminant (e.g., exposure over many years). Acute and sub-chronic refers to the health effects due to short term exposure to the contaminant (e.g., a single exposure to exposure over several weeks).

[E] HAL: Acute and sub-chronic Health Advisory Levels, as reported in USEPA, 1995b.

[F] Young, 1992.

[G] USEPA, 1995b.

[H] Opresko, 1992a.

[I] Francis and Forsyth, 1995.

[J] Daugherty, 1992a.

[K] Young, 1991.

[L] Daugherty, 1992b.

[M] Action level, not MCL, alerting the supplier to implement corrective actions under the Lead and Copper Rule.

[N] Faust, 1992a.

Table 3-1. Regulated Inorganic Contaminants (Cont.)

Contaminant	MCL & MCLG [A]	Chronic Oral RfD [B] and/or SF [C]	Potential Chronic Health Effects from Consumption Above the MCL [D]	HAL[E] 1-10d (≤ 7y)	Other Reported Acute/Sub-Chronic Doses	Potential Acute and Sub-Chronic Health Effects from Consumption Above the HAL [D]
Cyanide (CN^-), free	0.2 mg/L	RfD: 0.02 mg/kg/d	Weight loss, thyroid effects, and nerve damage. [G,O]	0.2 mg/l (0.2 mg/l)	50-100 mg as NaCN or KCN (collapse) [O]	Rapid breathing, tremors, other neurological effects. [G,O]
Fluoride (F)	4.0 mg/L 2.0 mg/L (SMCL)	None	Bone disease including pain/tenderness. Mottled teeth in some children. [Q]	None	150 mg/L [P]	Nausea, vomiting, diarrhea, abdominal pain, and paresthesias. [P]
Lead (Pb)	0.015 mg/L [M] 0 mg/L (MCLG)	None	Gastrointestinal disturbance, nervous, cardiovascular, kidney, and reproductive system damage and delays in physical or mental development in infants and children. [G,R]	None	Not Available	Gastrointestinal disturbance, nervous, cardiovascular, kidney, and reproductive system damage and delays in physical or mental development in infants and children. [G,R]
Mercury (Hg), inorganic	0.002 mg/L	RfD: 3x10^{-4} mg/kg/d [S]	Kidney, central nervous system, and gastrointestinal tract damage. [G,S]	None	1-4 g (lethal) [S]	Gastrointestinal pain, vomiting, diarrhea, hemorrhage, renal failure, shock, and cardiovascular collapse. [G,S]
Nitrate (NO_3^-), as N	10 mg/L	RfD: 1.6 mg/kg/d as N [T]	Diuresis, increased starchy deposits, and hemorrhaging of the spleen. [G]	10 mg/L	10 mg/L	Anoxia and death (Blue baby syndrome in infants under six months). [G,T]
Nitrite (NO_2^-), as N	1 mg/L	RfD: 0.1 mg/kg/d as N [U]	Diuresis, increased starchy deposits, and hemorrhaging of the spleen. [G]	1 mg/L	1 mg/L	Anoxia and death (Blue baby syndrome in infants under six months). [G,T]
Selenium (Se)	0.05 mg/L	RfD: 0.005 mg/kg/d	Selenosis, hair or fingernail loss, damage to kidney and liver tissue, and the nervous and circulatory systems. [G,V]	None	0.26 mg/kg/day (sub-chronic selenosis)	Selenosis, excessive salivation, shallow breathing, diarrhea, pulmonary edema, and death. [G,V]
Thallium (Tl)	0.002 mg/L 0.0005 mg/L (MCLG)	RfD: 6.7x10^{-5} mg/kg/d	Sleep disorders, tiredness, weakness, nervousness, headache, and neurological and muscular symptoms. [G,W]	0.007 mg/L (0.007 mg/l)	3-20 mg/kg (lethal) [W]	Gastrointestinal tract hemorrhage and gastroenteritis, hair loss, nervous system damage, convulsions, coma, and respiratory failure. [G,W]

[A] USEPA, 2003. The Maximum Contaminant Level (MCL) and the Maximum Contaminant Level Goal (MCLG) are identical unless stated otherwise. Secondary Maximum Contaminant Level (SMCL) is given if applicable.

[B] RfD: Chronic oral reference dose for non-carcinogenic toxic health effects based on findings of No Observable Adverse Effect Level (NOAEL) or Lowest Observable Adverse Effect Level (LOAEL).

[C] SF: Slope factor is the upper-bound incremental risk of developing cancer due to lifetime exposure to a particular unit intake.

[D] Chronic refers to the health effects due to long term exposure to the contaminant (e.g., exposure over many years). Acute and sub-chronic refers to the health effects due to short term exposure to the contaminant (e.g., a single exposure to exposure over several weeks).

[E] HAL: Acute and sub-chronic Health Advisory Levels, as reported in USEPA, 1995b.

[G] USEPA, 1995b.

[M] Action level, not MCL, alerting the supplier to implement corrective actions under the Lead and Copper Rule.

[O] Faust, 1994.

[P] Gessner et al., 1994.

[Q] USEPA, 2003.

[R] Davidson, 1994.

[S] Young, *Undated*.

[T] Francis, 1995.

[U] USEPA, 1997.

[V] Opresko, 1993.

[W] Borges and Daugherty, 1994.

Table 3-2. Unregulated Inorganic Contaminants

Contaminant	MCL & MCLG [A]	Chronic Oral RfD [B] and/or SF [C]	Potential Chronic Health Effects from Consumption Above the MCL [D]	HAL[E] 1-10d (≤ 7y)	Other Reported Acute/Sub-Chronic Doses	Potential Acute and Sub-Chronic Health Effects from Consumption Above the HAL [D]
Aluminum (Al)	0.05 to 0.2 mg/L (SMCL)	None	None found. [X]	NA	Not Available	None found. [X]
Manganese (Mn)	0.05 mg/L (SMCL)	RfD: 0.14 mg/kg/d	May cause neurological impairment. [Y]	1 mg/l (0.3 mg/l lifetime) [Y]	Not Available	Lethargy, increased muscle tonus, tremor, mental disturbances. [Y]
Nickel (Ni)	None {0.1 mg/L} [Z]	RfD = 0.02 mg/kg/d	Decreased body weight, heart and liver damage, and dermatitis. [G]	NA	Not Available	Nausea, vomiting, abdominal pain. [AA]
Silver (Ag)	0.10 mg/L (SMCL)	RfD = 0.005 mg/kg/d	Argyria (irreversible gray or blue-gray discoloration of skin & mucous membranes). [BB]	NA	Not Available	Corrosive damage to the gastrointestinal tract, abdominal pain, diarrhea, vomiting, shock, convulsions, and death. [BB]
Vanadium (V)	None	RfD = 0.007 mg/kg/d	Intestinal cramping and diarrhea. [CC]	NA	0.4-1.3 mg/kg/d [CC]	Intestinal cramping and diarrhea. [CC]
Zinc (Zn)	5 mg/L (SMCL)	RfD = 0.2 mgkg/d	Anemia. [DD]	NA	40 mg/kg (lethal) [DD]	Nausea, vomiting, diarrhea, abdominal cramps. [DD]
Rare Earth Elements (REE)	None			NA	Not Available	N/A

[A] USEPA, 2003. The Maximum Contaminant Level (MCL) and the Maximum Contaminant Level Goal (MCLG) are identical unless stated otherwise. Secondary Maximum Contaminant Level (SMCL) is given if applicable.

[B] RfD: Chronic oral reference dose for non-carcinogenic toxic health effects based on findings of No Observable Adverse Effect Level (NOAEL) or Lowest Observable Adverse Effect Level (LOAEL).

[C] SF: Slope factor is the upper-bound incremental risk of developing cancer due to lifetime exposure to a particular unit intake.

[D] Chronic refers to the health effects due to long term exposure to the contaminant (e.g., exposure over many years). Acute and sub-chronic refers to the health effects due to short term exposure to the contaminant (e.g., a single exposure to exposure over several weeks).

[E] HAL: Acute and sub-chronic Health Advisory Levels, as reported in USEPA, 1995b.

[G] USEPA, 1995b.

[X] Bast, 1993.

[Y] USEPA, 2004f.

[Z] The MCL and MCLG were remanded on 2/9/95. The USEPA is currently reconsidering the MCL. USEPA, 1995b.

[AA] Young, 1995.

[BB] Faust, 1992b.

[CC] Opresko, 1991.

[DD] Opresko, 1992b.

Table 3-3. Regulated Radiological Contaminants

Contaminant	MCL & MCLG [A]	HAL[E] 1-10d (≤ 7y)	Potential Chronic Health Effects from Oral Consumption Above the MCL [D]
Alpha Emitters	15 pCi/L (MCLG=0)	NA	Increased risk of cancer. [Q]
Beta and Photon Emitters	4 mrem/yr (MCLG=0)	NA	Increased risk of cancer. [Q]
Radium-226/228 (226Ra/228Ra), Combined	5 pCi/L (MCLG=0)	NA	Increased risk of cancer. [Q]
Radon (Rn)	None	NA	Increased risk of cancer. [Q]
Uranium (U)	30 µg/L (MCLG=0)	NA	Increased risk of cancer and kidney damage. [Q]

[A] USEPA, 2003. The Maximum Contaminant Level (MCL) and the Maximum Contaminant Level Goal (MCLG) are identical unless stated otherwise. Secondary Maximum Contaminant Level (SMCL) is given if applicable.

[D] Chronic refers to the health effects due to long term exposure to the contaminant (e.g., exposure over many years). Acute and sub-chronic refers to the health effects due to short term exposure to the contaminant (e.g., a single exposure to exposure over several weeks).

[E] HAL: Acute and sub-chronic Health Advisory Levels, as reported in USEPA, 1995b.

[Q] USEPA, 2003.

The following sections provide background information on each contaminant as it pertains to the potential for accumulation. This includes natural and anthropogenic factors that may influence contaminant occurrence in source waters potentially used for supply; other potential pathways into the distribution system; and the physical and chemical characteristics of contaminants as they typically exist within distribution systems that may affect their fate and transport.

3.1 Regulated Inorganic Compounds

Antimony

Naturally-occurring antimony exists in various ores which may release antimony to groundwater via erosion and dissolution. Specific ores that contain elevated levels of antimony include stibnite (sulfide) and valentinite (trioxide). Other ores containing antimony include cervantite, livingstonite, jamisonite, and kermesite (USEPA, 1995b). Antimony is also a common component of coal and petroleum.

With regard to anthropogenic sources, antimony is released to the atmosphere from industrial dust, auto exhaust, fuel oil, processing of antinomy materials, copper and lead smelting and refining, and molding and incineration of certain products. Antimony in the atmosphere may enter water sources through deposition in precipitation (USEPA, 1995a; USEPA, 1995b). Antimony may also leach out of tin-antimony solder if used within distribution systems.

In the aqueous environment, antimony typically exists in a hydrolyzed soluble form in one of two valence states: trivalent or pentavalent. Under reducing conditions, the trivalent species $Sb(OH)_3$ and $Sb(OH)_4^-$ predominate in the natural pH range. Under oxidizing conditions, the pentavalent species $Sb(OH)_6^-$ and $Sb(OH)_5$ predominate in the natural pH range (ATSDR, 1992a). Since these species generally have an anionic character, they are expected to have little affinity for organic carbon and clays. However, antimony is known to form co-precipitates with hydrous iron, manganese, and aluminum oxides in soil and sediment (Callahan et al, 1978). The concentration of antimony in natural waters is usually too low to generate oxide or sulfide precipitates.

Arsenic

Naturally-occurring arsenic is present in over 200 different mineral deposits, the most common being arsenopyrite (FeAsS). Mineral deposits may release arsenic to groundwater via erosion and dissolution processes. Arsenic is also released to the atmosphere through volcanic activity and may be returned to soils and natural waters through wet or dry deposition.

With regard to anthropogenic sources, releases may occur due to mining activity, combustion of fossil fuels, use of arsenical pesticides, herbicides and crop desiccants, and use as a wood preservative. Arsenic may also enter the distribution system water through leaching from cement linings, even when NSF approved materials and linings are applied according to AWWA standards (AWWA and EES, 2002b).

While arsenic can exist in a variety of oxidation states, the forms most commonly found in natural waters and soils are the soluble, acid-behaving oxyanions arsenite (AsO_3^{3-}) and arsenate

(AsO_4^{3-}). Arsenite exists under reducing conditions and is highly soluble and mobile due to its neutral net surface charge in the natural pH range. Arsenate exists under oxidizing conditions and has a negative surface charge in the natural pH range, thus enhancing its sorption/co-precipitation with various hydrous metal oxides, particularly those of iron and manganese (Smedley and Kinniburgh, Undated*;* Britton et al., 2003). As with other metal oxyanions, the sorption profiles are highly pH-dependant (Schock, 2005).

Barium

Naturally-occurring barium exists in various ores which may release barium to groundwater via erosion and dissolution processes. The most common barium ores are barite (barium sulfate) and witherite (barium carbonate). Barite occurs largely in sedimentary formations along with fluorspar and metallic sulfides, and is widely distributed in Alaska, Arkansas, California, Georgia, Kentucky, Missouri, Nevada, and Tennessee. Witherite is often associated with lead sulfide and is prevalent in Arkansas, California, Georgia, Kentucky, Missouri, and Nevada (USEPA, 1995b; Choudhury and Cary, 2001). Barium is also found in coal at concentrations up to 3000 mg/kg, as well as in fuel oils (IPCS, 1990; ATSDR, 1992b).

With regard to anthropogenic sources, barium is released to water and soil via mining activity, the discharge and disposal of drilling wastes, copper smelting activities, and the manufacture of motor vehicle parts and accessories (USEPA, 1995a; USEPA, 1995b). Barium may also enter the distribution system water through leaching from cement linings, even when NSF approved materials and linings are applied according to AWWA standards (AWWA and EES, 2002b).

In solution, barium typically exists in cationic form (Ba^{2+}). Depending on water quality conditions, it may form mineral precipitates involving carbonate, sulfate, and/or chromate (USEPA, 1995b). Even when undersaturated with respect to these mineral phases, barium may still be associated with various solid matrices. This is due to the positive charge of the barium ion, which aids in partitioning to hydrous metal oxide substrates, clay, and organic matter (Smedley and Kinniburgh, Undated*;* Schock, 2005).

Beryllium

Naturally-occurring beryllium can be found in mineral rocks, soil, coal, oil, and volcanic dust at levels ranging from 0.038 to 11.4 mg/kg (Drury et al., 1978). It is typically concentrated in silicate minerals relative to sulfides and feldspar minerals relative to ferromagnesium minerals. The greatest known naturally-occurring concentrations of beryllium are found in certain pegmatite bodies (USEPA, 1995b). Other beryllium minerals of significance are beryl, an aluminosilicate that contains up to 4% beryllium, and bertrandite, a beryllium silicate hydrate that contains less than 1% beryllium (Bruce and Odin, 2001).

With regard to anthropogenic sources, beryllium is released to the environment primarily from coal combustion. The beryllium content of the ashes and wastewater from a power plant suggest that secondary long-term beryllium pollution emerges from the slag and ash dumps. It is also found in discharges from other industrial and municipal operations. Rocket exhaust products may contain some of its compounds, principally the oxide, fluoride and chloride (USEPA, 1995b). Traces of beryllium may also leach out of tin-antimony solder if used within the distribution system.

In the natural pH range, beryllium tends to form insoluble oxide precipitates or hydrated complexes, thus limiting its dissolved concentration as cationic beryllium (Be^{2+}) to trace levels.

Cadmium

Naturally-occurring cadmium exists in various ores which may release cadmium to groundwater via erosion and dissolution processes, particularly in the presence of soft, acidic waters (USEPA, 1995b). Cadmium is typically associated with zinc ores (e.g., sphalerite), and to a lesser extent, with lead and copper ores. Other ores include greenockite (sulfide) and otavite (carbonate).

With regard to anthropogenic sources, cadmium is released to the environment primarily through the smelting and refining of zinc, lead, and copper ores (USEPA, 1995b). Other sources include waste incineration, wastes from electroplating operations, production of nickel-cadmium batteries, and fossil fuel combustion (Kazantzis, 1987). Cadmium may enter the water supply from the corrosion of galvanized pipes (USEPA, 1995b) or through leaching from cement linings, even when NSF approved materials and linings are applied according to AWWA standards (AWWA and EES, 2002b).

In solution, cadmium typically exists in divalent form as free cadmium (Cd^{2+}) or one of its hydrated forms (e.g., hexahydrate). It may also be complexed by various ligands such as humic acid and carbonate. Cadmium may form mineral precipitates involving oxides/hydroxides or carbonates, particularly at higher pHs. Even when undersaturated with respect to a mineral phase, cadmium may still be associated with various solid matrices. This is due to the positive charge of the cadmium ion and complexes, which aids in partitioning to hydrous metal oxide substrates, clay, and organic matter (Smedley and Kinniburgh, Undated). As with most cationic trace metals, sorption is typically enhanced at higher pH levels (Schock, 2005).

Chromium

Naturally-occurring chromium most commonly occurs in ores of chromite ($FeCr_2O_4$) and chromic oxide (Cr_2O_3), both of which are relatively insoluble. Weathering and *in situ* biological oxidation processes may convert trivalent forms of chromium to chromates (CrO_4^{2-}) which are more soluble and mobile in natural waters.

With regard to anthropogenic sources, chromium is used in a variety of industrial processes that release waste streams to the air and water. Higher values of chromium in the environment (and in particular hexavalent chromium) are typically associated with industrial releases (USEPA, 1995b). The two largest sources of chromium emission in the atmosphere are from the chemical manufacturing industry and combustion of natural gas, oil, and coal. Chromium in the atmosphere may enter surface water sources through deposition by precipitation (USEPA, 1995b). Chromium may also enter the distribution system water through leaching from cement linings, even when NSF approved materials and linings are applied according to AWWA standards (AWWA and EES, 2002b). There are also some cases of chromium entering the distribution system during cross-connection incidents with cooling towers or building heating systems where chromium is used as a rust and corrosion inhibitor (USEPA, 2002).

In solution, chromium typically exists in either trivalent or hexavalent form. The trivalent form (Cr^{3+}) generally exists under reducing conditions and is relatively insoluble and immobile due to precipitation as $Cr(OH)_3$. Hexavalent chromium (CrO_4^{2-}), which generally exists under oxidizing conditions, is a soluble oxyanion that behaves similar to arsenate (Smedley and Kinniburgh, Undated). The hexavalent form has a negative surface charge in the natural pH range, thus enhancing its sorption/co-precipitation with various hydrous metal oxides. As with other oxyanions, it sorption profile is highly pH-dependant (Schock, 2005).

Copper

Naturally-occurring copper exists in its elemental state as well as various mineral deposits, primarily as sulfides, carbonates, hydroxides, and oxides. Common copper-bearing minerals include azurite, malachite, chalcopyrite, bornite, covellite, chalcocite, antlerite, and cuprite. These compounds may release copper to groundwater via erosion and dissolution processes.

With regard to anthropogenic sources, copper is released to the environment primarily through the smelting and refining of copper, as well as municipal incineration. These releases may contaminate surface and groundwater sources supplying the distribution system (USEPA, 1995b). Copper is also commonly used for domestic and institutional plumbing and may enter the water supply from corrosion of plumbing systems (USEPA, 2003). Additionally, incidents of cross-connection or backflow of acids, most often carbon dioxide from soft drink dispensers, can release toxic amounts of copper into the drinking water system (USEPA, 2002).

In solution, copper typically exists in cationic form as either cuprous (Cu^{+}) or cupric (Cu^{2+}) species, depending on the oxidation-reduction potential. Both species may form mineral precipitates involving carbonate, oxide, hydroxide, or phosphate, though to differing degrees. The solubility of both species is also highly dependent on solution pH, with higher pH levels generally limiting solubility. At high dissolved inorganic carbon (DIC) levels, copper solubility may be enhanced by carbonate ligation (AWWA, 1999). Even when undersaturated with respect to a mineral phase, copper may still be associated with various solid matrices. This is due to the net positive charge of the soluble form, which aids in partitioning to hydrous metal oxide substrates, clay, and organic matter (Smedley and Kinniburgh, Undated*;* Schock 2005).

Cyanide

Cyanide is a chemical compound composed of a cyanogens group in combination with an element or radical. In water it is present as hydrocyanic acid (HCN), cyanide ion (CN^{-}), cyanides of metal cations, or it can be incorporated into an organic molecule (notably, cyanogen chloride, a disinfection byproduct). Cyanide is released to the environment primarily through discharges to water from metal finishing industries, iron and steel mills, organic chemical industries, and heap leach mining. These releases may contaminate surface and groundwater sources supplying the distribution system (USEPA, 1995b). Cyanide is relatively mobile in the natural environment.

A related issue is that the partial chlorination of cyanide results in the formation of cyanogen chloride, an equally toxic but unregulated compound. To eliminate the cyanide from the finished water without creating cyanogen chloride, the cyanide must be oxidized with chlorine at a pH of 8 or greater (USEPA, 1994).

Fluoride

Fluoride is the anionic form of fluorine, an extremely reactive and corrosive gas in its free form. Fluorine forms fluorides with almost all known elements. Fluoride may enter the water supply from the erosion of natural deposits, through the intrusion of waste runoff from fertilizer or aluminum factories, or through purposeful addition to the finished water for dental health (USEPA, 2003).

In solution, fluoride typically exists as an anion (F^-) given the water quality conditions typically found in distribution systems. Fluoride may partition to metal oxide substrates, particularly those of alumina (Britton et al., 2003).

Lead

Lead is a heavy, malleable, metal rarely found in elemental form in nature. It occurs principally in minerals of carbonate (cerrusite), sulfate (anglesite), sulfide (galena), and oxide (plattnerite). These compounds may release lead to groundwater via erosion and dissolution processes.

With regard to anthropogenic sources, lead may be derived from atmospheric fallout, runoff, or wastewater from mining, ore processing, smelting, refining use, recycling, or disposal. Although some lead does enter the distribution system through the source water, most lead contamination is from corrosion of plumbing materials (USEPA, 1995b).

In solution, lead typically exists as either divalent ($Pb^{2+)}$ or quadravalent (Pb^{4+}) species, depending on the oxidation-reduction potential. Lead may form mineral precipitates involving carbonate (e.g., cerrusite), hydroxide (e.g., lead hydroxide), hydroxycarbonate (e.g., hydrocerrusite), oxide, or phosphate. The solubility behavior of the two forms of lead differs; however, both are highly dependent on solution pH, with higher pH levels generally limiting solubility. At high DIC and high pH, lead solubility may be enhanced by carbonate ligation (AWWA, 1999). Even when undersaturated with respect to a mineral phase, lead may still be associated with various solid matrices. This is due to the net positive charge of the soluble forms in the natural pH range, which aids in partitioning to hydrous metal oxide substrates, clay, and organic matter (Smedley and Kinniburgh, *Undated;* Schock, 2005).

Mercury

Mercury is the only common metallic element found as a liquid at ambient temperatures. In the environment it rarely occurs in a free state, but typically in combination with sulfur. Noticeable amounts of mercury are released naturally from the earth’s crust due to weathering. Waterborne mercury pollution tends to originate in sewage, metal refining operations, and chloralkali plants (USEPA, 1995b). Mercury may enter the drinking water system through the source water.

Nitrate/Nitrite

Nitrite and nitrate can be introduced into water distribution systems directly via the source water. They can also potentially be formed within distribution systems through the bacterially-mediated oxidation of organic nitrogen and/or ammonia compounds.

Although nitrogenous compounds can be released in ambient waters as a result of natural processes, the impact of these sources is generally minimal (AWWA and EES, 2002a). The primary sources of nitrogen compounds are source water contamination with agricultural runoff from fertilization or livestock wastes or contamination from sewage (USEPA, 1995b). Also, the precursor ammonia may be intentionally added as part of the disinfection process to produce chloramines.

Selenium

Selenium is a metalloid that usually occurs in sulfide ores, heavy metals, and minerals such as eucairite (CuAgSe), crookesite (CuTlSe) and clausthalite (PbSe). These compounds may release lead to groundwater via erosion and dissolution processes.

With regard to anthropogenic sources, selenium compounds are released to the air during the combustion of coal and petroleum fuels, and during the smelting and refining of some metals (USEPA, 1995b). Selenium in the atmosphere may enter surface water sources through deposition by precipitation.

In natural waters, selenium typically exists as the acid-behaving oxyanions selenous acid/selenite (SeO_3^{3-}) and selenic acid/selenate (SeO_4^{3-}). Selenous acid/selenite exists under reducing conditions and has a negative net surface charge in the natural pH range, thus enhancing its sorption/co-precipitation with various hydrous metal oxides (Smedley and Kinniburgh, Undated). As with other oxyanions, it sorption profile is highly pH-dependant (Schock, 2005). Selenic acid/selenate exists under oxidizing conditions and is more soluble and mobile than its reduced counterpart due to its neutral net surface charge in the natural pH range.

Thallium

Thallium is a metallic element that is widely distributed in nature and is a trace metal associated with ores of copper, lead, zinc, and sulfides. Thallium is primarily found in the minerals crookesite ($TlCu_7Se_4$), hutchinsonite ($TlPbAs_5S_9$), and lorandite ($TlAsS_2$). These compounds may release thallium to groundwater via erosion and dissolution processes.

With regard to anthropogenic sources, thallium may be release to the environment through gaseous emissions from cement factories and coal burning power plants. The leaching of thallium from ore processing operations is the major source of elevated thallium concentrations in water (USEPA, 1995b). Thallium may also enter the water supply from intrusion of waste runoff or deposition by precipitation.

In solution, thallium typically exists in cationic form as either thallous (Tl^{1+}) or thallic (Tl^{3+}) species. The monovalent form is more common, though the trivalent form may exist under highly oxidizing conditions. Both forms are highly soluble in natural waters, but may adsorb onto organic-rich soils, sediments, and clays (ATSDR, 1992c).

3.2 Unregulated Inorganic Compounds

Aluminum

Aluminum is an unregulated metallic element that occurs naturally in groundwater and soil due to the erosion of aluminum-bearing minerals.

Aluminum-based salts are often used as a chemical coagulant in drinking water treatment plants. Depending on flocculation and treatment efficacy, and pH perturbations within the distribution system, aluminum may concentrate in the distribution system due to post-precipitation of coagulant residual (Snoeyink et al., 2003). Aluminum may also enter the distribution system water through leaching from cement linings, even when NSF approved materials and linings are applied according to AWWA standards (AWWA and EES, 2002b).

In solution, aluminum exists in trivalent form as free aluminum ion (Al^{3+}) or one of several hydrated complexes. Depending on water quality conditions, aluminum may form mineral precipitates involving hydroxide, oxide, or phosphate. Its solubility behavior is highly pH-dependant, with minimum solubility typically occurring around pH 6.5. Even when undersaturated with respect to a mineral phase, aluminum may still be associated with various solid matrices. This is due to the net charge of the soluble form, which aids in partitioning to hydrous metal oxide substrates, clay, and organic matter (Schock, 2005).

Manganese

Manganese is an unregulated metallic element that occurs naturally in compounds found in soil, air, water and food. Human exposure occurs primarily through ingestion of foods containing manganese and may also occur through inhalation of dust or intake of soil or drinking water containing manganese (USEPA, 2003). Manganese occurs widely at detectable levels in public water sources; however, when considered with intake from a normal diet, drinking water normally represents a relatively small proportion of total manganese intake (USEPA, 2003).

Regarding anthropogenic sources, manganese is released to the environment primarily from production of manganese-iron alloy through a smelting process, and as an ingredient in fertilizers, fungicides, livestock feed and gasoline additives (USEPA, 2003b).

In solution, manganese typically exists in one of three forms, depending on oxidation-reduction potential: manganous (Mn^{2+}), manganic (Mn^{4+}), or permanganate (Mn^{7+}). The manganous and permanganate forms are highly soluble and mobile, whereas the manganic forms will readily precipitate as manganese oxide (MnO_2). Hydrous manganese oxides have been shown to be effective scavenging agents for certain trace inorganics, including lead, arsenic, and radium (Schock, 2005).

Nickel

Nickel is an unregulated metallic element found abundantly in nature in various mineral ores as sulfides, arsenides, antimonides, oxides, and silicates. These compounds may release nickel to groundwater via erosion and dissolution processes.

With regard to anthropogenic sources, nickel is released to the environment primarily from nickel smelting/refining and steelworks operations (USEPA, 1995b). Some reports have also indicated that nickel may leach out of plumbing materials into the system water (Nielsen and Anderson, 2001).

In the aqueous environment, nickel typically exists in cationic form either as free nickel (Ni^{2+}) or hydrated forms (e.g., nickel hexahydrate), both of which are highly soluble. At higher pH levels, it may form a mineral precipitate involving oxide/hydroxide or carbonate (ATSDR, 2005a). Due to the positive charge of the soluble forms in the natural pH range, nickel may partition to various hydrous metal oxide substrates, clay, or organic matter (Smedley and Kinniburgh, Undated; Schock, 2005).

Silver

Silver is an unregulated metallic element. In nature, silver occurs primarily in the form of the sulfide (Ag_2S) or associated with other metal sulfides, especially those of lead, copper, iron, and gold. These compounds may release nickel to groundwater via erosion and dissolution processes.

With regard to anthropogenic sources, silver may be released to the environment by the processing of ores, steel refining, fossil fuel combustion, and municipal waste incineration. Silver may enter the water supply from intrusion of waste runoff or absorption in precipitation.

In the aqueous environment, silver typically exists in cationic form as free silver (Ag^+), and to a lesser degree, as complex ions involving chloride and sulfate. Both forms are highly soluble. Silver may form mineral precipitates involving oxides or phosphates, particularly at higher pH levels. Due to the positive charge of the soluble forms, silver may also partition to various hydrous metal oxide substrates, clay, and/or organic matter. In particular, significant quantities of silver may be absorbed by manganese oxides (ATSDR, 1990a).

Vanadium

Vanadium is an unregulated metallic element that occurs in six oxidation states. Most vanadium produced is used as an alloying agent, but is also used as catalyst. In the natural environment, vanadium exists in over 50 different mineral ores. Vanadium may enter the water supply through erosion of natural deposits or, to a lesser extent, contamination of source water by waste runoff.

In natural waters, vanadium typically exists in one of two valence states: quadravalent (V^{4+}) or pentavalent (V^{5+}). The quadravalent species VO^{2+} and $VO(OH)^+$ predominate in the natural pH range under reducing conditions. The pentavalent species $H_2VO_4^-$ and HVO_4^{2-} predominate in the natural pH range under oxidizing conditions (ATSDR, 1992d). These species readily partition to hydrous metal oxide substrates, particularly those of iron and manganese, as well as organic matter. Depending on substrate availability and solution pH, a substantial amount of vanadium may be solids-associated rather than soluble.

Zinc

Zinc is an unregulated metallic element used primarily for galvanizing metal alloys to reduce corrosion. Although zinc can enter the distribution system with the source water, its presence is more likely to be the result of corrosion of plumbing materials. Zinc may also be introduced into the distribution system through chemical additions such as zinc orthophosphate.

In solution, zinc typically exists in divalent form as free zinc cation (Zn^{2+}) or as hydrated ions (e.g., $Zn(OH)_3^-$), depending on the pH. It may also be complexed by various organic ligands. It may form mineral precipitates involving oxides/hydroxides or carbonates, particularly at higher pH levels. Due to the generally positive charge of the soluble form in the natural pH range, zinc may also partition to various hydrous metal oxide substrates, clay, or organic matter (ATSDR, 2005b).

Rare Earth Elements

The rare-earth elements (REE) are scandium (Sc), yttrium (Y), and the 15 elements on the periodic table between and including lanthanum (La) and lutetium (Lu) including dysprosium (Dy). These elements are all trivalent and have very similar chemical properties. Rare earth elements may enter the water supply through contamination by waste runoff or absorption and precipitation.

3.3 Regulated Radiological Compounds

Alpha Emitters

Alpha emitting radioactive elements, also known as alpha emitters, emit an alpha particle during radioactive decay. Alpha particles are large subatomic fragments, identical to a helium nucleus having two protons and two neutrons. There are many alpha emitting radioactive elements, both natural and man-made. The primary alpha emitters are: americium-241, plutonium-236, uranium-238, thorium-232, radium-226, radon-222, and polonium-210 (USEPA, 2004c). Alpha emitters may enter the water supply either dissolved in the source water or attached to turbidity particles in the source water.

Beta and Photon Emitters

Beta emitting radioactive elements, also known as beta emitters, emit a beta particle during radioactive decay. Beta particles are subatomic particles, equivalent to electrons, ejected from the nucleus of some radioactive atoms. The primary beta emitters are: tritium, cobalt-60, strontium-90, technetium-99, iodine-129 and -131, and cesium-137 (USEPA, 2004d). Beta and photon emitters may enter the water supply either dissolved in the source water or attached to turbidity particles in the source water (USEPA, 2003) or through cross connections (USEPA, 2002).

Often, gamma ray photon emission accompanies the emission of a beta particle. When the beta particle ejection does not rid the nucleus of the extra energy, the nucleus releases the remaining excess energy in the form of a gamma photon. Because of their high energy, gamma photons travel at the speed of light and can cover hundreds to thousands of meters in air before spending their energy. They can pass through many kinds of materials, including human tissue (USEPA, 2003).

Radium

Radium in nature is composed of four isotopes: ^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra (Focazio et al., 2001). The two most prevalent isotopes of radium, ^{228}Ra and ^{226}Ra, are progeny of separate decay series, which has important implications with regard to occurrence and mobility. ^{228}Ra is the second member of the ^{232}Th decay series, has a half-life of 5.75 years, and decays via beta particle emission. ^{226}Ra is the fifth member of the ^{238}U decay series, has a half-life of 1,622 years, and decays via alpha particle emission into ^{222}Rn. ^{224}Ra is the fifth member of the ^{232}Th decay series, has a half-life of 3.64 days, and decays via alpha particle emission into ^{220}Rn. ^{223}Ra is a member of the ^{235}U decay series and rarely occurs in the environment at high activities. The latter two are generally of little interest in drinking water applications.

Radium may enter the water supply either dissolved in the source water or attached to turbidity particles in the source water (USEPA, 2003a). The occurrence of radium in groundwater depends largely on the presence and solubility of the respective parent elements (Focazio et al., 2001). In general, ^{226}Ra is more widely distributed than ^{228}Ra due in part to the fact that its parent element, ^{238}U, is more soluble and mobile than ^{232}Th. Elevated levels of ^{226}Ra are particularly widespread within the northern-central region of the United States, which is attributable to deep geologic formations of Cambrian and Ordovician sandstones and dolomites and Cretaceous sandstones (Focazio et al., 2001). Elevated levels of ^{226}Ra are also found in aquifers that straddle the Fall Line from Georgia to New Jersey, which are composed of unconsolidated sands that contain fragments of uranium-bearing minerals and sands derived from the crystalline rocks of the Blue Ridge, Piedmont, and parts of the Coastal Plain physiographic provinces (Focazio et al., 2001). The potential for ^{228}Ra is closely related to the occurrence of thorium, which is prevalent in aquifers of arkosic sand and sandstone (Longtin, 1988).

Radium in water exists primarily as a divalent ion (Ra^{2+}) and has chemical properties similar to barium and calcium (all radium isotopes behave similarly). The concentration of radium in water is typically governed by pH-controlled adsorption/desorption reactions at various solid matrices, as well as co-precipitation reactions with barium (ATSDR, 1990b).

Radon

Radon is a naturally-occurring radioactive gas that has no color, odor, or taste. There are two isotopes of radon, ^{222}Rn and ^{220}Rn; however, the latter has historically been of little interest in drinking water because its half-life is only 55 seconds (and that of its parent element ^{224}Ra is also relatively short at 3.6 days). As used in the literature, radon generally refers to ^{222}Rn, which has a half-life of 3.8 days, is a progeny of ^{226}Ra, and is part of the ^{238}U decay series.

Radon may enter the distribution system dissolved in the source water. It may also be formed in the distribution system from the radioactive decay of radium either in the bulk water or accumulated on deposits or corrosion byproducts within the system. The occurrence of radon in groundwater is generally correlated with the geologic occurrence of its parent compounds, including ^{238}U and ^{226}Ra. In general, high levels of radon are associated with granite igneous rocks, dark shale, sedimentary rocks that contain phosphates, metamorphic rocks derived from these rocks, and phosphate deposits and ores, as these rocks and their soils may contain as much as 100 mg/kg of uranium (USGS, Undated).

Uranium

Uranium is a naturally-occurring radioactive metallic element that is commonly found in very small amounts in rocks, soil, water, plants, and animals (including humans). Naturally-occurring uranium contains approximately 99.27% ^{238}U, 0.72% ^{235}U, and 0.006% ^{234}U (OEHHA, 2001).

Naturally-occurring uranium is derived from the erosion of uranium-bearing rocks and minerals. The following formations generally contain high uranium content: granite, sedimentary rocks (e.g., shale), metamorphic rocks derived from these rocks, and phosphate deposits, minerals, and ores (e.g., lignite, monazite sands) (USGS, Undated; Cothern and Lappenbusch, 1983). Naturally-occurring uranium is also released into the aqueous environment from various activities such as the use of phosphate fertilizers, mining, and combustion from coal and other fuels. Uranium may enter the water supply either dissolved in the source water or attached to turbidity particles in the source water (USEPA, 2003).

In the natural environment, uranium typically exists in one of two valence states, depending on oxidation-reduction potential: quadravalent (U^{4+}) or hexavalent (U^{6+}). The quadravalent form exists under reducing conditions and tends to form relatively insoluble and immobile precipitates. The hexavalent form, also known as uranyl, typically exists under oxidizing conditions and is more soluble due to the formation of ionic hydroxo- and carbonato-complexes (ATSDR, 1999). It can also be complexed by organic ligands. Uranium and has been shown to migrate through groundwater systems as extremely small colloids of varying compositions, including rare-earth element phosphates, iron oxyhydroxides, clays, or iron-coated clays (Schock, 2005). The extremely small size of these colloids is of potential concern in drinking water because they can readily pass through treatment processes. Uranium exhibits sorptive affinity for hydrous oxides of iron and manganese.

4.0 Overview of Inorganic Contaminant Reservoirs

The contaminants described in the previous section may accumulate on or within materials commonly found within water distribution systems. The materials that support contaminant accumulation are referred to as contaminant reservoirs. For the purposes of this paper, these contaminant reservoirs have been categorized as scales, biofilms, or sediments, listed in order of rigidity of attachment to the pipe surface. In reality, scales, biofilms, and sediments often occur in a complex and dynamic matrix that reflects a variety of factors influencing their formation, as well as patterns of inorganic contaminant accumulation and release.

Friedman et al (2003) identified "control variables" that directly impact the quantity and nature of deposits within distribution systems. Figure 4.1 illustrates the complexity of the relationships governing the accumulation of deposits and the presence of contaminant reservoirs within distribution systems. The top row represents the control variables that can be theoretically identified and controlled by a water utility. The second row represents secondary variables, which are considerably more difficult to evaluate and quantify. Flow arrows were used to define the presence of a significant relationship between sets of variables in both rows. While Figure 4.1 was originally developed to assess flushing effectiveness, the underlying goal of distribution system flushing is to remove accumulated materials and contaminant reservoirs, such as scales, biofilms, and sediments.

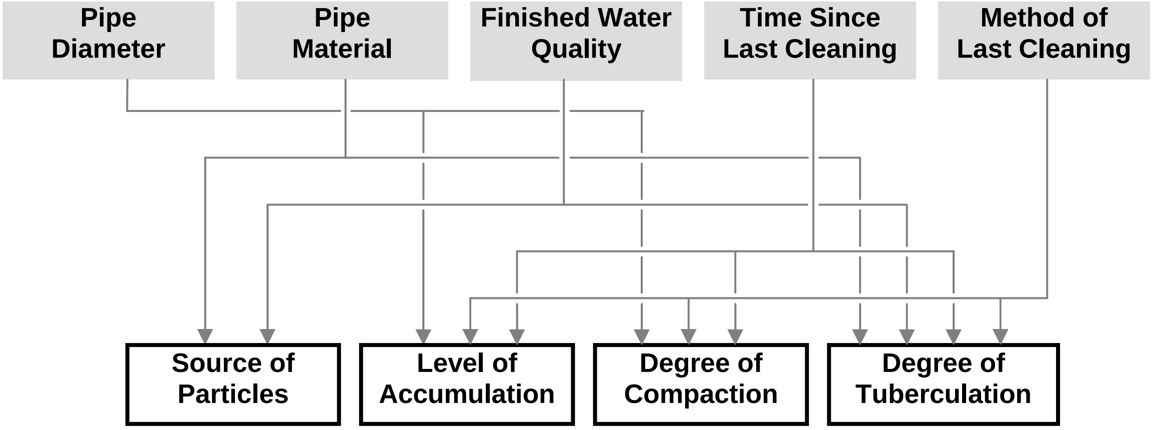

Figure 4-1. Variables Impacting Deposit Accumulation and Contaminant Reservoirs (Adapted from Friedman et al. 2003).

Sections 4.1, 4.2, and 4.3, provide an overview of scales, biofilms, and sediments, including representative means of formation, composition and related background information.

4.1 Scales

Scales may be (1) corrosion products that form on pipe surfaces, (2) deposits that form as a result of the precipitation of contaminants (precipitation scales) from the distribution water, or (3) combinations of both. Corrosion scales form as a result of the degradation of metallic surfaces by an electrochemical reaction. Precipitation scales form in response to changes in water quality.

Both corrosion and precipitation scales represent a reservoir of inorganic materials in and of themselves. In addition, some scales have the ability to attract and bind inorganic contaminants that are present in distribution water. As a result, scales represent a concentrated reservoir of inorganic constituents that, if dislodged, re-solubilized, or otherwise released back into the distribution water, they can result in contaminant concentrations that temporarily exceed drinking water standards or secondary guidelines for aesthetics (Clement et al., 2002; Clement and Carlson, 2004).

Reiber et al. (1997b) note that water distribution systems consist of a variety of metal surfaces, including steel, cast and ductile iron, zinc, copper, lead, and a number of specialty alloys. Many of these metals are used because of their overall corrosion resistance. Nonetheless, all metal surfaces form a corrosion scale unique to the metal type. The authors further note that corrosion scales consist largely of the oxidized metal, but will generally contain constituents such as calcite and other minerals.

The corrosion resistance and scale formation characteristics of construction materials used in distribution systems varies. For example, overall corrosion resistance is generally good for copper pipe and fixtures. However, it is subject to corrosive attack from high water velocities, soft water, chlorine, dissolved oxygen, and low pH. Lead pipe corrodes in soft water with low pH leading to potential contamination from lead, arsenic, and cadmium. Turbidity and red-water complaints are often the result of corrosion of mild steel piping (i.e., steel having a carbon content less than 1.5% that does not harden thoroughly and is weldable) caused by high dissolved oxygen levels. Typically, the corrosion is uniform across the surface of the mild steel pipe. Similar iron corrosion problems can occur from the erosion of cast or unlined ductile iron pipe by aggressive waters. Galvanic corrosion of zinc by aggressive waters can occur with galvanized iron pipe leading to the release of zinc and iron (Grayman et al., 2000).

Chemical Composition of Scales

The affinity of scales for accumulating various types of inorganic contaminants depends in part on chemical composition of the scale. This section describes the composition of scales and the inorganic contaminants that have been observed to be associated with them.

Schock (2004) reviewed the literature on distribution systems as reservoirs for the accumulation of inorganic contaminants and noted that corrosion scales associated with ductile and cast iron pipes are frequently oxides, oxyhydroxides, hydroxycarbonates, carbonates, and hydroxysulfates. Benjamin et al. (1996) provide a simplified schematic showing the mineralogical profile typical of corrosion products in cast iron pipes.

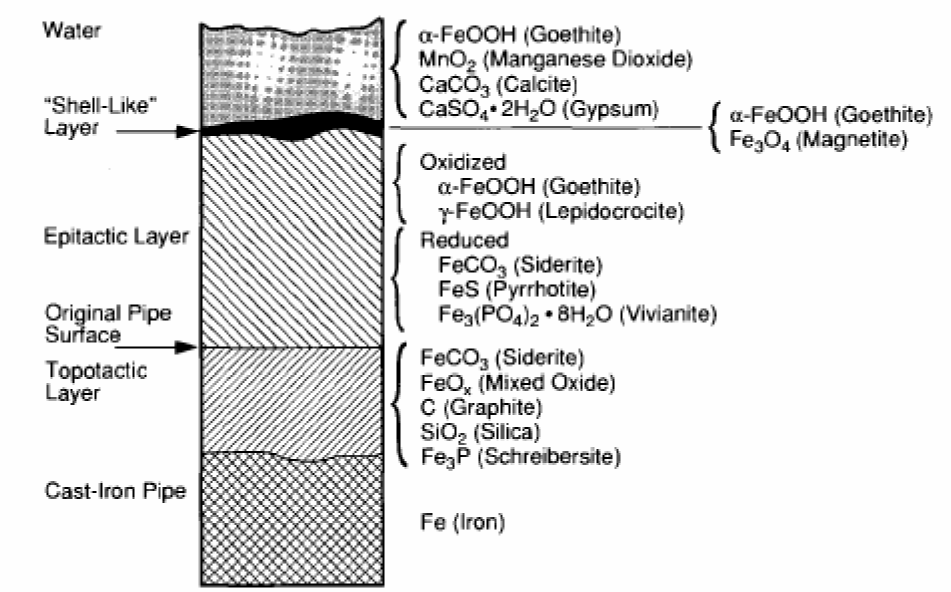

Figure 4-2. Profile of Typical Cast Iron Corrosion Scale (from Benjamin et al., 1996)

As part of a research investigation to develop red water control strategies, another study analyzed iron scales of pipelines from two locations and found that most of the scale was in the form of Fe (II). Some was in crystalline forms (most commonly goethite and magnetite). No siderite was detected (Clement, et al. 2002). Scale containing $Fe(OH)_2$ was also reported in distribution systems with very soft, low-alkalinity water (Sontheimer et al., 1981).

Benjamin, et al. (1996) investigated the corrosion of iron and steel pipes and the formation of iron scales. Low-alkalinity waters produced iron scales that were thick (~ 2-3 cm) and loose, with a dark orange-brown crust containing flecks of yellow-colored scale that could be easily cracked to expose a soft, porous, black or greenish-black interior. The scale formed tubercles that could be easily scraped off. In contrast, scales from high-carbonate waters were thin, hard, and tightly bound to the metal surface. They appeared as dark brown patches of fairly uniform thickness ($\leq$ 1 mm).

Kirmeyer et al. (2000b) reported on the chemical composition of scales from cast iron, galvanized iron and lead pipe based on pipe samples from several utilities. For the cast and galvanized iron scales, magnetite and goethite were found, but not siderite. Sulfur and chloride were also found in samples from one system; silica was found universally. Lead scale was primarily hydrocerrusite ($Pb_3(CO_3)_2OH$), with some aluminum and silica present. Aluminum was found in scales from two systems and was believed to be present from the use of aluminum sulfate for coagulation because one utility reported that the aluminum residuals in the finished water from one of its two plants would predictably increase during the summer when source water pH rose above 8.0, and that post-precipitation within the distribution system was likely as pH was reduced due to blending.

Cuprous (Cu I) and cupric (Cu II) forms of copper that are produced during the corrosion of copper pipe result in both insoluble precipitates and soluble complexes. The precipitates may form scales or be present as blue or green suspensions in water. The complexed forms contribute soluble copper to the water and also affect the solubility of deposited scales (Ferguson et al., 1996). Pipe loop studies by Benjamin et al. (1990) documented that a small fraction of the scale formed from copper corrosion was cuprite (Cu_2O). The fraction was slightly higher in high-pH water (pH 8.0) than in low-pH water (pH 6.0). The presence of cupric oxide (CuO) and hydrated cuprous oxide ($Cu_2O \cdot H_2O$) was suspected, but could not be confirmed.

Snoeyink et al. (2003) analyzed the composition of aluminum-containing scales from several utilities using aluminum-based coagulants but different corrosion control approaches and concluded that post-precipitation of aluminum was occurring. A literature review conducted as part of the study showed that scale composition could include aluminum oxides, hydroxides, phosphates and silicates. Aluminosilicate deposits may also form from the corrosion (leaching) of cementitious material (e.g., mortar lined pipe) (Schock, 2004).

Factors Influencing Scale Formation

Corrosivity of Water. Corrosion scales form as a result of the degradation of metallic surfaces by electrochemical reactions. Schock (1990) provides a very detailed and comprehensive background of the science of corrosion in drinking water. He notes that corrosion results from the flow of electric current between anodic and cathodic areas on the metallic surfaces of a distribution system. The anodic and cathodic areas may be microscopic and in close proximity, leading to generally uniform corrosion, or large and somewhat remote from one another, leading to pitting with or without tuberculation.

Corrosion scales are most prevalent in "aggressive" waters – those commonly associated with one or more of the following conditions (Lane, 1993):

- Soft waters.
- Low pH and alkalinity.
- High chloride and/or sulfate.
- Appreciable dissolved oxygen.
- Low buffer intensity.
- Low pH and high conductivity.
- High chlorine residual.

However, even waters reported to be "noncorrosive" can have corrosive (and therefore scale-forming) properties. Differences are only a matter of degree (Lane, 1993).

Water Hardness and Alkalinity. Hardness, principally from calcium and magnesium ions, can lead to scale formation. Precipitation scale formation can be beneficial in that, if managed, it can inhibit corrosion; however, if not managed, hard waters can form severe precipitation scale (calcium carbonate) with a resulting reduction in the hydraulic friction factor and pipe capacity. (Kirmeyer et al., 2000a; Lane, 1993). In a scale-forming water, the potential for release of accumulated contaminants would likely be reduced. However, if scale reducing/dissolving chemicals are added, the captured inorganic chemicals (IOCs) could potentially be released.

Alkalinity is a measure of the capability for water to neutralize acids (Clement et al., 2002). For iron corrosion, lower alkalinities can correspond to higher corrosion rates. As discussed previously, Benjamin, et al. (1996) found that, in comparison with high alkalinity waters, low alkalinity produced soft, thick scales on iron and steel pipes, which could release accumulated inorganic contaminants. For groundwater sources or sources with high alkalinity (above 100 mg/L) and high calcium levels (above 50 mg/L as $CaCO_3$), increases in pH above 8.0 can result in calcium carbonate precipitation (Kirmeyer et al., 2000a). Alkalinity and calcium concentrations are the predominant factors that determine the calcium carbonate saturation pH (Economic and Engineering Services et al., 1990).

Water Chemistry Changes. Changes in alkalinity-pH relationships in water significantly affect corrosivity and, therefore, scale formation. These relationships are complex and depend on water quality factors such as pH level, alkalinity concentration, and DIC.

Lack of pH stability, typically caused by inadequate alkalinity and DIC and, therefore, low buffer intensity, can lead to low pH values that enhance corrosive properties. In some cases, changes in pH of as much as 2 pH units throughout the day have been observed. The pH of poorly buffered waters in contact with asbestos cement or cement-lined pipe can increase to 10 or higher, possibly damaging the pipe lining. Lead corrosion rates can be increased under some pH conditions and with increases in alkalinity/DIC.

Utility case studies conducted as part of a nationwide survey also confirmed the importance of pH stability, or lack thereof, on corrosion and scale formation on lead and iron pipe (Reiber et al., 1997b). The importance of pH stability on lead levels found at a major northeast utility has also been reported (Clement et al., 1998). Clement et al., (1998) documented significant reductions in lead levels through corrective actions that included increasing the pH from 7.8 to 9.2 and increasing the DIC from 1.7 mg/L to 7 mg/L. The corrective actions also reduced the range of monthly pH variation from 2 pH units to <0.5 pH units.

The presence of trace organics in water has been reported to affect the nature of scale formation on a variety of metallic surfaces (Campbell, et al. 1983). This research study found that the presence of trace organics tended to promote deposition of thin, uniform carbonate scales rather than nodular forms. The presence of trace organics was also found to stabilize the pH of carbonate rich waters and thereby prevent significant pH reduction with its attendant increase in corrosivity.

Oxidation/Reduction Potential. Disinfectant residual type and concentration, dissolved oxygen (DO) concentration, and pH can all impact oxidation-reduction potential (ORP). The ORP at the pipe-water interface can have a significant impact on corrosion properties and mineralogy of the scale.

Schock et al. (1996) reported that differences in DO concentrations on different areas of a pipe surface can produce galvanic concentration cells and influence the rate of corrosion of lead piping. Schock et al. (1995) reported on detailed experimental studies that document the influence of DO, residual chlorine, and stagnation time on copper pipe corrosion. The authors noted that in the presence of an oxidizing disinfectant residual and/or dissolved oxygen, oxidation and solubilization of copper would occur until either the saturation index of a passivating layer (e.g., $Cu(OH)_2$) was reached or the disinfectant residual and DO were depleted.

ORP plays a significant role in the composition and stability of scales. One study (Benjamin et al., 1990) found that, in keeping with the model of Sontheimer et al. (1981), siderite ($FeCO_3$) was present to some degree in all of the protective films formed on steel pipes analyzed. It was noted that siderite formation is enhanced when ferrous ion is not rapidly oxidized to ferric ion. Moderately alkaline, high-carbonate, highly buffered waters favor siderite formation. Thus, increased ORP in the water may limit the formation of siderite scales and associated corrosion protection.

Significant effects of chlorine on ORP and attendant changes in the nature of predominant lead-containing scales and their solubility have also been observed (Lytle and Schock, 2005; Vazquez et al., 2006). Davis et al. (2005) noted the effect of chlorine concentration on copper scale conversion from cupric hydroxide to tenorite.

Piping Materials. As noted above, although piping materials vary in their corrosion and scale-forming characteristics, all metal surfaces form corrosion scales to some degree. Characteristics are unique to the metal type (Reiber et al., 1997b; Grayman et al., 2000). The chemical composition of scales formed by corrosion is highly variable and dependent on the pipe material. Thus, iron and steel pipes yield a variety of corrosion products, including those in the ferrous and ferric states, those in crystalline structures, and several that are combined with species such as carbonates, hydroxides, sulfates, and chlorides.

Tubercles are formed inside pipes by the corrosion process and are formed of corrosion products. Their composition is determined by many factors, including pipe material. Clement et al. (2002) performed detailed elemental analysis of tubercles found on 80-year-old galvanized iron pipe and 90-year-old unlined cast iron pipe. In both types of pipe, the tubercles were composed of primarily iron. Additionally, the researchers found that the galvanized pipe tubercles contained significant amounts of, in descending order: silicon, zinc, copper, and calcium. The unlined cast iron pipe tubercles also contained sulfur.

Lead pipe corrosion yielded a lead carbonate (hydrocerrusite) as the primary corrosion scale in one study (Kirmeyer et al., 2000b). Corrosion of copper piping produces both insoluble precipitates (i.e., scale) and soluble complexes in cuprous and cupric states (Ferguson et al., 1996; Benjamin et al., 1990).

On some metal surfaces scales may be quite thin – copper pipe scale thickness is often less than 0.2 mm. On cast iron surfaces the scales can be voluminous, frequently exceeding a depth of 1 cm. In even a relatively small distribution system the existing scales will contain several tons of metal oxides, while in large systems the corrosion scales represent a massive reservoir of metals best measured in the kiloton (Reiber et al., 1997b).

Another study found indications that aluminosilicate deposits may form from the leaching of cementitious material such as that used in mortar-lined pipe (Schock, 2005).

Zacheus et al. (2001) determined that pipeline deposits obtained via mechanical system cleaning were the primary location of microbes in four distribution systems. These deposits were composed of (in descending order) iron, carbon, calcium, aluminum, and manganese. Additionally, significant levels of copper, nickel, phosphorus, and zinc were present. Delanoue et al. (1997) used a pipe rig to study pipe deposit formation. The researchers studied new pipes of different materials and found that, over three years, deposit accumulation was highest in exposed iron pipes. The researchers ranked pipe materials according to deposit accumulation (highest to lowest): exposed iron, bitumen, epoxy, cement and MDPE, and glass (Delanoue et al. 1997).

4.2 Biofilms

Biofilms are defined in the Distribution System White Paper (USEPA, 2002) entitled *Health Risks from Microbial Growth and Biofilms in the Distribution System* as a "complex mixture of microbes, organic and inorganic material accumulated amidst a microbially-produced organic polymer matrix attached to the inner surface of the distribution system." Biofilms are present in many distribution systems and often include bacteria that can be found in source water. There are two general areas of concern associated with biofilms and inorganics accumulation/release:

- The potential for biofilms to entrain and accumulate/release inorganic contaminants, and

- The potential for the release of biofilm pathogens when the distribution system sediment/biofilm/scale complex is disturbed.

A third and interrelated area of interest is associated with the biomass accumulated *within* corrosion scales and tubercles. This material is not typically considered "biofilm" since it is not "attached" to the inner surface of the distribution system, rather, it can form an integral part of corrosion tubercles themselves. Corrosion tubercles often contain sulfur-reducing and iron bacteria, in addition to other microorganisms. In a study conducted by Tuovinen et al. (1980), tubercle deposits collected from pipelines in the Columbus, Ohio, water system were examined to characterize bacteria, chemical composition, and minerals present. The complex environment favors a variety of biological and chemical interactions. Many types of bacteria were present: sulfate reducers, nitrate oxidizers, ammonia oxidizers, sulfur oxidizers, and unidentified aerobic heterotrophic bacteria. Filamentous organisms, coliforms and iron oxidizers were not detected.

A study by Emde et al (1992) assessed microbial growth in corrosion tubercles in a cold-water distribution system, where year-round water temperatures remain near zero degrees Celsius. The study found a heterogeneous population of potentially corrosive microorganisms present in untreated supply water, treated water and corrosion tubercles. This included sulfite-reducing bacteria (*Clostridium* species), sulfate-reducers; iron-reducing bacteria (*Bacillus* species, *Clostridium* sp., *Escherichia coli*, *Enterobacter aerogenes*, *Klebsiella oxytoca*, *Klebsiella pneumoniae, Pseudomonas aeruginosa, Pseudomonas cepecia, Pseudomonas fluorescens*), sulfur-oxidizing bacteria (*Thiobacillus thiooxidans, Thiobacillus thioparus*), iron-precipitating bacteria (*Leptothrix, Gallionella, Sphaerotilus*), sulfate-reducing actinomycetes and iron-reducing fungi (Penicillium, Rhizopus, Aspergillus). In this study, the authors noted that corrosion tubercles contained greater numbers of coliforms than did the untreated supply or treated water. The authors concluded that the ability of corrosion tubercles to sustain a diverse population of direct and opportunistic pathogens may be an unrealized vector in the transmission of certain waterborne diseases to potential risk groups.

For the purposes of this paper, the discussion of biofilms is limited to the first area concern described above, i.e., the potential for biofilms to entrain and accumulate/release inorganic contaminants. While it is recognized that the chemical or physical destabilization of corrosion scales can release biofilm organisms into the bulk water, the potential public health impacts associated with biofilm disturbances are discussed in the Distribution System White Paper prepared by USEPA (2002) entitled *Health Risks from Microbial Growth and Biofilms in the Distribution System.* Although related to scale stability and release of inorganic contaminants, the potential health risks associated with release of biologically active material from within corrosion tubercles constitutes a separate research topic worthy of further investigation.

With respect to drinking water biofilms, much of the research to date has been focused on analyzing the types of bacteria present, organic nutrients within biofilms and associated with formation, and biofilm control through disinfection or other means. Less information is available on the presence of inorganic compounds found in biofilms and the accumulation and release of these compounds by biofilms. Available information is summarized below.

Biofilms can sorb water, organic and inorganic solutes, and particles. Sorption sites include cell walls, cell membranes, cell cytoplasm and the extracellular polymeric substances (EPS) itself, all of which display different sorption preferences, capacities and properties. This situation is complicated even more as biofilms respond physiologically to sorbed substances. For example, the uptake of toluene can lead to the formation of uronic acids in the EPS and, thus, to an increased sorption capacity for cations (Flemming, 1995). Costerton and Lapin-Scott (1989) also found that the EPS can entrain nutrients. Dissolved and sediment-attached IOCs may be entrained by the EPS and accumulate in a similar manner.

Hanjangsit et al. (1994) found that biofilms grown on stainless steel contained detectable levels of molybdenum and nickel, possibly originating from the stainless steel. Percival et al. (1997) found that biofilm age and water temperature could significantly impact the capability of biofilms to accumulate metals. Researchers detected nickel in biofilm samples grown on stainless steel and fed by a hot water source but did not detect nickel on samples fed by a cold water source. In the same study, metals were not detected in biofilms established for five months, but were present in those established for 10 or more months (Percival et al.,1997).

Some bacteria can produce a slime that creates corrosive organic acids (AWWA, 2004). Another common example of bacteria that may be present in drinking water biofilms is iron-precipitating bacteria (iron bacteria). These bacteria convert Fe^{2+} (soluble iron) to Fe^{3+} (iron precipitate), which is then deposited outside of the bacterial cells. Iron bacteria are not harmful to public health, but are considered to be nuisance microbes since they can precipitate large quantities of iron (AWWA, 2004). The resulting iron precipitation can cause taste and odor problems, frothing, color, and increased turbidity. Additionally, iron biofouling can cause reduced flow in the distribution system and lead to deterioration of distribution system piping.

Iron and manganese precipitating bacteria can accumulate large amounts of precipitate in relation to their biomass (AWWA, 2004). Sly, Hodgkinson, and Avunpairojana (1990) studied manganese deposition in drinking water distribution systems. In one distribution system, manganese-depositing biofilm significantly increased total manganese levels in the distribution system. For instance, during a one week period without the presence of a disinfectant residual, total manganese levels rose from approximately 0.02 mg/L to 0.08 mg/L (Sly, Hodgkinson, and Avunpairojana, 1990).

Microbiologically influenced corrosion (MIC) of copper is an example of biofilm causing corrosion and releasing inorganic compounds into drinking water. MIC can produce areas of green film on the pipe surface, tubercles which cover jagged-edged pits, and, eventually, pinholes (Cantor et al., 2003). Using a simulated distribution system, Webster et al. (2000) noted that copper pipe corrosion was enhanced by biofilm-induced conditions at the pipe-water interface, that the presence of a biofilm made the protective oxide layer more porous and weaker than that developed without a biofilm present, and that higher-than-anticipated levels of copper may be associated with accumulation of copper by-products in biofilm.

Bremer et al. (2001) point out that bacteria such as *Sphingomonas* spp., and *Pseudomonas fluorescens*, can accumulate copper in their cell walls. Bremer and Geesey (1991) found that a noncorrosive biofilm could protect the copper pipe from corrosion, preventing corrosive types of bacteria from colonizing the area and causing corrosion. If conditions do become too toxic for the biofilm layer, copper release could also be caused by biofilm sloughing from the pipe surface and entering the bulk water.

According to Schock (2005), certain bacterial biofilm materials in natural aquatic environments have been observed to influence the transport and fate of heavy metals. Nelson and colleagues (1995) gives a good example for lead, in which both cells and extracellular polymeric material attached to the iron substrate were responsible for immobilizing lead.

Factors Influencing Biofilm Formation

Since biofilms can accumulate IOCs, factors influencing biofilm formation, such as those that enhance growth or cause sloughing, also impact the uptake and release of IOCs in the distribution system. Biofilm formation is dependent on a complex interaction of water quality, infrastructure, and operational factors associated with distribution systems (Volk and Joret, 1994; LeChevallier et al., 1991; LeChevallier et al., 1996).

The thickness and composition of drinking water biofilms is not necessarily uniform in time and space, and depends on changes in water quality, temperature, flow dynamics, pipe age, pipe material and individual installation (Bachmann, *Undated*). Within the distribution system, areas of corrosion and slow flow provide the most attractive sites for biofilm development. Reservoir and standpipe sediments, as well as sidewalls, are also attractive sites (Grayman et al., 2000). The Distribution System White Paper (USEPA, 2002) entitled *Health Risks from Microbial Growth and Biofilms in the Distribution System* describes biofilm formation and control practices in detail.

4.3 Sediments

Sediments are loose particulate matter that accumulates in the low-velocity zones, dead ends, and reservoirs of distribution systems. Sediments may be comprised of silt, dirt, and organics from raw water sources, minerals such as iron and manganese, corrosion by-products from the distribution system, treatment by-products, or organic matter and cell debris which grow and detach in the distribution system. Over time, sediments may remain loose, become cohesive or compacted, or adhere to pipe surfaces. If sediments remain loose, they may travel within the distribution system due to changes in flow velocity and/or direction. This section presents a general review of sediment accumulation in water distribution systems and factors affecting these accumulations.

Composition of Sediments

Sediments occur within pipelines and storage facilities to some degree in all systems. Because of their long residence time, storage facilities have the potential to accumulate significant amounts of sediment. The composition of sediments depends on the source(s) contributing to the accumulation. The source water can provide a continuous supply of sediments, such as inorganic contaminants and organic matter attached to turbidity. This is particularly true for high-turbidity groundwater sources that have the potential to introduce water with turbidities in the range of more than 1.2 NTU to the distribution system. Some of these ground water sources may have recently been designated as Ground Water Under the Influence of Surface Water. As such, additional treatment is required, which may include practices that reduce turbidity. However, if these sources have been in operation for many years, it is possible that significant levels of sediment may have already accumulated within the distribution system.

Sediments that include corrosion products that have broken away from pipeline surfaces will have many, if not all, of the characteristics of the scale itself. Precipitation scales or products in sediments will likewise have characteristics similar to those of the original material. Corrosion scales, precipitation scales, and coalesced turbidity having contaminants sorbed from the distribution water will have compositions that reflect the characteristics of the particulates and sorbed contaminants. Particulates that enter the distribution system inadvertently, e.g., from main breaks, will have a variety of characteristics.

Block et al. (1996 in Kirmeyer et al., 2000a) collected sediment samples from finished water storage facilities and water mains and determined their composition, as shown in Table 4-1. From the table, it can be seen that iron oxides and aluminum hydroxides comprised 19% and 15% of the sediment from the storage facilities, respectively, whereas iron oxides comprised 62% of the water main sediments and aluminum hydroxides were not detected. In both cases, calcium carbonates made up about 10% of the sediment and the volatile component was 14-19% of the total.

Table 4-1. Comparison of Sediment Composition.

Storage Facility Sediment	Water Main Sediment
Insolubles—18%	Insolubles—3%
Iron oxides—19%	Iron oxides—62%
Volatile solids—19%	Volatile solids—14%
Aluminum hydroxides—15%	Calcium carbonates—9%
Calcium carbonates—10%	Unknown—8%
Unknown—10%	

Source: Block et al. (1996) in Kirmeyer et al. (2000a).

DeRosa (1993) conducted a survey of distribution system deposits encompassing 71 supply zones in the United Kingdom. The field surveys showed that there was a large variation in the quantity of deposits in water mains within supply zones. Even mains of similar size and type and in close proximity showed large variations in quantities of loose deposit present. It was suggested that local features (e.g. hydraulics) of the water mains had a significant effect on particle deposition and accumulation. Relatively more deposits were found in small diameter mains (≤ 4 inches) at the ends of distribution systems, an observation attributable to the occurrence of low flow regimes at these sites. However, large diameter mains (≥ 6 inches) did contain sediment. Statistical analysis indicated that lowland reservoirs and river sources (which tend to contain more fine sediment from overland runoff) were associated with more distribution deposits than upland reservoirs and groundwater well sources. The compositional analysis of the deposits collected in hydrant nets produced a list of seventeen elements. The predominant elements were iron (13-45% of the sample), aluminum (2-45%), phosphorus (0.1-18%), calcium (0.5-17%), and manganese (0.2- 6%).

Carrière et al. (2002) conducted unidirectional flushing in four Canadian distribution systems and evaluated the accumulated loose deposits as a function of time, pipe material and water characteristics. The quantity and nature of the deposits varied greatly among the various networks and sampling campaigns and sampling times. The principal factors affecting deposit accumulations were the accumulation period, the pipe material, and the corrosivity of the water.

Systems with little or no flushing/cleaning programs and significant amounts of unlined ductile iron may have significant levels of deposits.

Friedman et al. (2003) analyzed distribution system deposits collected in hydrant nets (57 to 308 µm size range) during flushing trials conducted at five utilities. Two unique flushing velocities were assessed at each location to determine if higher velocities erode deeper into the sediment/biofilm/scale complex and release more and/or different accumulated materials. The purpose of conducting low velocity flushing (i.e., less than 4 feet per second) was to remove loose deposits (sediments) and loosely attached deposits. The purpose of higher velocity flushing (i.e., greater than 5 feet per second) was to remove attached scales and tubercles. Table 4.2 summarizes the iron content of particles removed during the two discrete flushing velocity trials.

Table 4-2. Iron Fraction of Distribution System Deposits

Site	Pipe Type	Velocity fps (m/s)	Particle Iron Fraction
ANC	Asbestos-Cement	3.8 (1.2)	29.6 %
		6.0 (1.8)	30.2 %
BEL	Asbestos-Cement	4.0 (1.2)	59.7 %
		7.6 (2.3)	56.3 %
CLE	Cement Lined Cast Iron	3.0 (0.9)	33.3 %
		5.9 (1.8)	37.6 %
NNI	Ductile Iron	2.6 (0.8)	46.4 %
		6.6 (2.0)	18.6 %
POR	Unlined Cast Iron	3.4 (1.0)	22.6%
		6.1 (1.9)	57.4 %

Adapted from Friedman et al. (2003).

These data show that the two flushing velocities yielded significantly different iron results for two utilities, NNI and POR. For NNI, the iron fraction dropped 60% between the low and high velocity flushes, indicating that a greater fraction of accumulated iron-containing material was removed from this system at the lower velocity. Conversely, for POR the iron fraction increased by 154% between the low and high velocity flushes, indicating that the higher velocity flush penetrated deeper in the scale/biofilm/sediment complex, perhaps exposing the pipe surface. The particles removed during the low and high velocity flushes for ANC, BEL, and CLE appear to be similar in chemical nature. These findings are significant to this paper because they suggest that particles with differing composition may be yielded from the same stretch of pipe, depending on the particle collection technique (i.e., flushing velocity). Methods of monitoring to determine contaminant accumulation are described further in Section 9.

Post-precipitation of aluminum following source water treatment with aluminum-based coagulants can form sediments in distribution reservoirs and pipeline systems. Based on scale sample analysis from 10 water utilities that practice alum coagulation, Snoeyink et al. (2003) confirmed that aluminum is frequently a major component of lead pipe scale. Snoeyink et al.

(2003) also reference several previous studies that establish that post-precipitation of aluminum is responsible for deposits on the inner surface of distribution system piping. Re-suspension of the precipitate can contribute high concentrations of aluminum to the bulk water (Snoeyink et al., 2003).

Factors Influencing Sediment Formation

Turbidity. Coalescence of turbidity in source waters can result in accumulation of sediment in distribution systems. Often, inorganic and radiological contaminants are adsorbed to the colloidal turbidity particles (Clement and Carlson, 2004). One report notes that sediment loading rates are typically higher from sources without source water filtration, and that sediment loading rates often vary seasonally and proportionally to turbidity levels. Air-borne sand, dust and other particulates that settle in open reservoirs can lead to higher sediment loads than with covered storage facilities. (Kirmeyer et al., 2000a).

Flow Velocity. Sediments accumulate where flow velocities are reduced to levels allowing particles or chemical precipitates to settle by gravity. Friedman et al. (2003) found that the specific gravities of particles collected during distribution system flushing ranged from 2.5-3.5, with an average of 2.9, regardless of the source water or pipe material. With respect to in-pipe velocities, Friedman et al (2003) described water mains with typical velocities greater than 4 ft/s as “self-cleaning” because sediment typically does not accumulate at these velocities.

Oxidation/Reduction Potential. An increase in the ORP, e.g., with an increase in dissolved oxygen level in the bulk water, can convert reduced inorganics normally in a dissolved state to oxidized forms that can precipitate to form sediment layers on pipe surfaces or scales, as discussed previously. One example of this is the precipitation of iron and manganese that can occur when groundwater sources having elevated levels of these constituents in a reduced state are introduced into the oxidizing regime of the distribution system (Kirmeyer et al., 2000a).

Mechanical Disturbances. Sediment can be created by removing scale from the pipe wall. This removal can be caused by hydraulic phenomena such as increased water flow (e.g., fire flow), flow reversals, or transient pressure changes (e.g., water hammers) that shear the scale off of the pipe wall. Other mechanical disturbances would include construction and maintenance activities such as valve or pipe replacement or valve exercising. These activities are know to “stir up” loose deposits in distribution system networks, often leading to customer complaints.

4.4 Sediment/Scale/Biofilm Complex

Sections 4.1, 4.2, and 4.3 have provided an overview of each type of inorganic contaminant reservoir (scales, biofilms, and sediments, respectively). In many locations, particularly in the pipeline environment, each of the reservoirs does not exist independently. Rather, they are interconnected in a sediment/scale/biofilm complex. The accumulation of contaminants onto the sediment/biofilm/scale complex in the distribution system is a complicated chemical, physical, and sometimes biochemical process. These processes are also dynamic, which can result in continuous or intermittent accumulation and release of contaminants depending on system-specific and site-specific conditions. The degree to which each reservoir develops independently or as a complex is not well understood at this time. Thus, the degree to which each reservoir independently or as a tri-fold complex accumulates and/or releases inorganic contaminants is not well understood at this time. Future research will help further the understanding of this complex process.

5.0 Potential Factors Leading to Accumulation of Contaminants

Section 4 described factors that lead to development of each of the inorganic contaminant reservoirs (scales, biofilms, and sediments). Section 5 describes the factors that lead to accumulation of inorganic contaminants within the reservoirs. Because the reservoirs themselves can serve as contaminant sources if they are physically, chemically, or biochemically altered, several of the accumulation and release mechanisms are described in both Sections 4 and 5.

There are many factors that influence the extent of inorganic accumulation within distribution systems. First, the mechanisms of contaminant accumulation are summarized. Next, the factors leading to accumulation have been separated into two broad categories: 1) contaminant reservoir composition and mineralogy, and 2) water chemistry.

5.1 Mechanisms of Contaminant Accumulation

Inorganic contaminants accumulate in each individual reservoir or the sediment/biofilm/scale complex through a variety of physiochemical mechanisms including: sorption, absorption, adsorption, ion-exchange, chemisorption, metabolization, precipitation, and co-precipitation. The most likely mechanism varies depending on the accumulation location (i.e., pipeline environment or storage facility) and the type of reservoirs or reservoir complex present.

Sorption

Sorption is a general term used to encompass a number of processes including absorption, adsorption, desorption, ion exchange, and chemisorption (Parker, 1984). Sorption sites for biofilms include cell walls, cell membranes, and the EPS.

> ***Absorption***. Absorption is the penetration of a substance into the bulk of a solid or liquid (Parker 1984). This mechanism would be most applicable to accumulation of inorganics in biofilms and scales. The inorganic contaminants within the sediment may be captured by the EPS and absorbed into the biofilm. Dissolved contaminants penetrate scales and are absorbed. The permeation of a contaminant into a biofilm may be considered absorption.
>
> ***Adsorption***. Adsorption is the surface retention (or accumulation) of material (Parker, 1984). The forces that cause the attraction between the material and the surface can either be physical (e.g., van der Waals forces), electrostatic (coulombic forces), or chemical bonds (ionic or covalent).
>
> ***Ion-exchange***. Ion-exchange is a chemical reaction in which ions attached to a solid are exchanged with ions in solution (Parker, 1984). The process is reversible, and therefore ions in solution can accumulate in association with solids.

Chemisorption. Chemisorption is chemical bonding (either ionic or covalent) between the component and the surface material (Drever, 1997 in Bachmann, *Undated*). Chemisorption is generally an irreversible reaction (whereas ion-exchange is readily reversible). Chemisorbed contaminants are typically released through physical processes such as shear or sloughing, rather than through chemical processes.

Desorption. Desorption is the loss of a previously sorbed material by the reverse of adsorption or absorption (Parker, 1984). Desorbed materials can later be accumulated through one of the mechanisms described above.

Metabolization

Microorganisms use nutrients present in the environment for cell growth and energy production (Madigan et al., 2000). In particular, chemolithotrophs use inorganic compounds as energy sources and expel resulting waste products. For instance, iron-precipitating bacteria convert soluble iron (II) to a more insoluble form as iron (III), which is then deposited on or outside of the bacteria cells.

Precipitation

Precipitation is the process of producing a separable solid phase within a liquid phase (Parker, 1984). Some common contaminants in the bulk drinking water (e.g., iron, manganese, calcium, and aluminum oxides and carbonates) are frequently at concentrations high enough to precipitate. Chemolithotrophs can precipitate iron and manganese on the outside of their cells.

Co-precipitation

Co-precipitation is the precipitation of a normally soluble component with another insoluble component, resulting in the formation of mixed crystals. Many contaminants of potential concern may co-precipitate with the more common contaminants mentioned under precipitation.

With the exception of chemisorption, sorption is typically a reversible phenomenon. When the physiochemical conditions favor desorption, the contaminants will desorb from their sorption site and reenter the bulk water. Although co-precipitation can be reversible, it is generally more difficult for co-precipitated contaminants to desorb because many of them are occluded or trapped within the matrix of the sediment/biofilm/scale complex and are not on the surface available for desorption.

In general, most of the scale, biofilm, and sediment formation and contaminant accumulation occurs as the result of one or more of the physiochemical mechanisms listed. Because it is difficult to determine which mechanisms are the prevalent ones, the specific mechanism(s) are generally not determined and are referred to collectively as sorption.

5.2 Impact of Contaminant Reservoir Composition and Mineralogy

The extent of contaminant accumulation and later release of contaminants is strongly affected by the composition and the mineralogy of the contaminant reservoir.

The mineralogy of scales and sediments has been shown to affect the selectivity and amount of contaminants that can be adsorbed or co-precipitated. One example is the difference between green rust II and lepidocrocite iron oxide types, which have sorptive capacities towards uranium of 48,000 and 68,000 mg per kg of iron, respectively (Dodge et al., 2002).

This section describes the sorptive capacity of various components of contaminant reservoirs found in distribution systems.

Iron

It has been shown under laboratory conditions that the maximum adsorptive capacity of ferric hydroxide for arsenic at a pH of 7 and arsenate concentrations of up to 5 mg/L is 80,000 mg As per kg $Fe(OH)_3$ (Reiber et al., 1997a). Uranium species were found to strongly associate with the surfaces of many different iron oxide and oxyhydroxide corrosion products (Dodge et al., 2002) and was found to co-precipitate with iron oxides (Duff et al., 2002). Iron oxide sorptive capacities for radium have been found between 20-650 pCi/g of iron.

Based on the analysis of iron-rich solids collected from hydrant flushing and pipe samples from eight different utilities, one study concluded that accumulation of iron solids in distribution systems can concentrate arsenic even when arsenic is in the water at levels below 10 µg/L (Lytle et al., 2002). Another study (Lytle et al., 2004) showed that arsenic accumulation in pipelines from several utilities could be due to the presence of arsenic on iron carryover solids from the source water or from the adsorption of arsenic in the bulk water onto pipeline corrosion products.

Manganese

Hydrous manganese oxides have been shown to be important in adsorbing dissolved trace metals such as lead (Dong et al., 2003) and arsenate (Ouvrard et al., 2002) from natural waters and even in removing radium from drinking water (Valentine et al., 1990). The scavenging properties of manganese oxides are so good that it forms the basis for the use of MnO_2 precipitation as an analytical method to remove and preconcentrate trace metals such as aluminum, cadmium, copper, nickel, lead, vanadium, zinc, and rare earth elements (Umashankar et al., 2002). It has been shown under laboratory conditions that the maximum adsorptive capacity of manganic oxide for arsenate at a pH of 7 and arsenate concentrations of 5 mg/L is 1 mg As per kg MnO_2 (Reiber et al., 1997). Manganese oxide sorptive capacities for radium have been found between 20,000-40,000 pCi/g of Mn (Valentine and Stearns, 1994).

Aluminum

Aluminum oxides and aluminosilicates are also well known for their ability to adsorb trace metals, anions, oxyanions, and organic matter (Schock, 2005).

Copper

It has been shown under laboratory conditions that the maximum adsorptive capacity of cupric oxide for arsenic at a pH of 7 and arsenate concentrations of up to 5 mg/L is 180,000 mg As per kg $Cu(OH)_2$ (Reiber et al., 1997).

Biofilms

Biofilms provide various sorption sites such as the extracellular polymeric substances, cell walls, cell membranes, and cytoplasm. These sites display different sorption preferences, capacities, and properties (Flemming, 1995).

5.3 Water Chemistry

Water chemistry plays an important role in determining whether or not contaminants will accumulate, which contaminants accumulate, and to what extent the accumulation occurs. Water chemistry factors that can influence contaminant accumulation are discussed below.

Bulk Water Concentration

A higher contaminant concentration in the source/finished water tends to favor its accumulation by precipitation and/or sorption processes. Also, contaminants that readily leach or dissolve from materials or linings used within a system have a greater likelihood of accumulating.

Concentration of Competing Ions

Although contaminant reservoirs can be enormous, there are still a finite number of sorption sites. Each contaminant competes with other constituents in the water for the limited number of sorption sites. A high concentration of competing constituents will reduce the capacity of the reservoir for a particular contaminant.

Hill (2004) studied the competition effects on various iron oxide, iron oxyhydroxide, and iron-impregnated alumina substrates specifically engineered for drinking water arsenic treatment applications, noting that the oxyanions vanadate, chromate, silicate, and phosphate demonstrated competition with arsenate. Schock (2005) also cites several studies where phosphates, silicates, and sulfates have shown to be favorably sorbed by goethite and ferric hydroxide substrates, providing competition with intended arsenate sorption.

Concentration of Inhibitors and Sequesterants

Orthophosphate inhibitors react with lead, copper, calcium, and magnesium to form an insoluble coating on the internal surfaces of the distribution system (American Chemistry Council, 2004). This reduces metal leaching and the amount of corrosion scale that forms on the piping. The orthophosphate precipitates can also serve as a reservoir for inorganics accumulation. Jackson and Valentine (1995) demonstrated the affinity of orthophosphate precipitates for ^{226}Ra in pipe loop studies using simulated groundwater. The authors noted that the addition of orthophosphate to groundwater containing 1.0 mg/l of iron resulted in a 210% increase in the ^{226}Ra activity in the resulting solids compared to iron-containing groundwater without phosphate addition. Similarly, the addition of orthophosphate to groundwater containing varying levels of calcium (0 to 160 mg/l) consistently resulted in solids with very high ^{226}Ra activity, in the range 3,000 to 8,000 pCi/g. In the absence of orthophosphate, this same water yielded calcium carbonate precipitates with very little incorporated ^{226}Ra activity, in the range 80 to 141 pCi/g.

Polyphosphate sequesterants are used by some utilities to control discoloration resulting from the precipitation of iron and manganese originating from source water. It is often used in cases where source water iron and manganese levels exceed their respective secondary MCLs. However, under certain circumstances (such as with heat and over time), polyphosphate sequesterants can revert back to orthophosphates, allowing the complexed metals to precipitate and re-accumulate elsewhere in the distribution system. Depending on the iron and manganese concentrations in the source water and the stability of the sequestered complexes, these situations can potentially serve as a significant source of iron and manganese precipitates. These precipitates could serve as reservoirs for accumulation of regulated contaminants.

Concentration of Chelating Agents

Chelating agents such as NOM can ligate or complex with various inorganic contaminants in the bulk water and prevent their precipitation and potential deposition within the distribution system. In addition, organic ligands can bind to metal oxide reservoirs where they can provide a binding ligand site for trace metals in solution, which could increase accumulation. Such binding can also have the opposite affect by competing with direct sorption of the contaminants, which could decrease accumulation.

At the same time, NOM has been determine to affect the morphology and possibly composition of many typical solids phases found in distribution systems, notably calcite, hydrocerussite and malachite, thus also potentially affecting the accumulation potential (Korshin et al. 1996; Korshin et al. 2000; Hoch et al., 2000). Its role in the kinetics of accumulation of scales and sediments as well as in their mobilization remains to be explored in more detail.

pH

Water pH can influence the rate, selectivity, and extent (capacity) of inorganics accumulation via sorption processes by influencing the electrostatic properties and interactions of inorganic contaminants and distribution system scales. Most soluble inorganic contaminants within distribution systems exist as ions whose net surface charge is dependent on pH. Similarly, the surface charge of metal oxide scales and deposits depends on pH, with lower pH values producing a net positive charge and higher pH values producing a net negative charge, both relative to the zero-point-of-charge (pH_{zpc}) for the specific substrate. The pH_{zpc} for iron oxide and hydroxide substrates is typically in the range 7.5 to 8.5, while alumina-based substrates typically have a lower pH_{zpc}. The relationship between pH and sorption selectivity and equilibrium capacity is complex and depends on the specific substrate and bulk water quality conditions (Schock, 2005).

In addition to affecting sorption equilibria, water pH can also impact the solubility equilibria of inorganic contaminants and various precipitates that act as accumulation reservoirs, as has been explored in Benjamin (2002) and Dzombak and Morel (1990). For example, the solubility of cationic trace metals such as lead, copper, cadmium, and chromium (III) typically decreases with increasing pH (Smedley and Kinniburgh, Undated).

Oxidation/Reduction Potential

As discussed in Section 4, ORP can have a significant impact on the mineralogy and solubility of scales. In general, more reducing conditions favor increased metal solubility while more oxidizing conditions favor metal precipitation. In addition to influencing the stability of the reservoir itself, changes in scale composition can impact accumulation processes based on sorption and/or co-precipitation. For example, Schock (2005) notes that arsenic mobility is intimately related to the mineralogy of iron in the scales.

As discussed in Section 3, ORP can also affect contaminant properties, including valence state, surface charge, and the potential for sorption/co-precipitation. As an example, an increase in the residual chlorine concentration will increase ORP and will oxidize arsenite to arsenate (Britton et al., 2003). Because arsenate has a negative surface potential in the natural pH range, it is more readily adsorbed onto hydrous iron oxides.

Mixing of Waters

The mixing of different finished water sources and qualities (e.g., ground and surface water) within the distribution system can also affect contaminant accumulation. The blended water chemistry quality may alter precipitation or reservoir sorption patterns relative to the individual unmixed waters.

5.4 Formation of Contaminants within the Distribution System

There are some contaminants that do not physically accumulate in the distribution system, yet levels at the tap may be much higher than those at the entry to the distribution system. The more common of processes contributing to this phenomenon are nitrification and radioactive decay. Nitrification is the microbially mediated process of converting ammonia to nitrite and nitrate. Nitrite and nitrate formation within the distribution system is addressed in a separate white paper (AWWA and EES, 2002a).

Radioactive Decay

Radioactive elements that enter the distribution system may accumulate. If these elements then decay, they may produce daughter products in concentrations above the concentrations entering the distribution system. The most notable example of this is radon. Because radon is a noble gas and will not sorb easily, it will not accumulate in the distribution system. However, radon is a daughter product of radium decay (both ^{226}Ra and ^{228}Ra). If radium accumulates in the distribution system, the radium decay will result in concentrations of radon in the drinking water at the tap that are significantly higher that the radon levels entering the distribution system. An example of this is provided in the Case Study of Iowa Towns, 1991 and 1994 discussed in Section 7.

6.0 Potential Factors Leading To Release of Contaminants

Inorganic contaminants that accumulate in the sediment/biofilm/scale complex can be released back to the bulk water in a number of ways. Sections 6.1 and 6.2 present physical and chemical factors that influence the release of contaminants.

6.1 Physical Release of Contaminants

Accumulated contaminants may be physically released back into the water supply as particulates. This occurs when the contaminant reservoirs (i.e., the material the contaminants co-precipitated with or are sorbed to) are dislodged from the distribution system surfaces. Described below are several factors that have and/or could lead to the physical release of accumulated contaminants.

Increased Flow

Scales and biofilms are attached to distribution system surfaces with varying degrees of tenacity. Additionally, loose sediments may become compacted or adhered over time. Increased velocities resulting from increased flows (e.g., flushing, peak demands, and fire flows) can dislodge scale and biofilm and stir up accumulated sediments. The degree to which this occurs will depend on many factors including the magnitude of the velocity change, the rate of change, the location of the accumulation, and the nature of the accumulation. For example, Friedman et al. (2003) conducted experimental flushing trials and found that velocities of 1.7 to 1.9 fps could lift loose deposits of sand, while velocities of 1.6 to 2.4 fps were required to lift loose deposits composed of iron corrosion products. When flushing is conducted at higher velocities (i.e., above 4 fps), it was not possible to determine the origin of the particles removed, as they may have been loose sediment, compacted sediments, entrained in biofilm, or scoured from the pipe wall (Friedman et al. 2003). Controlled unidirectional flushing can be a beneficial maintenance practice in that it can help remove hydraulically-mobilizable contaminants that may be otherwise entrained during flow disturbances. Conventional hydrant flushing may remove some accumulated material, but it can also degrade bulk water quality by stirring up deposits without their removal.

The nature of the scale is important. For example, tubercles and similar encrustations and scales formed by pitting are likely to have portions that can be readily broken away by large and rapid changes in flow/velocity, while portions still remain intact at the pipe surface. Scales that are attached without significant corrosion of the pipe surface are likely to have break-away characteristics that are different from those that corrosively attack the metal surface itself. Examples are cited by Benjamin et al., 1990. In this pipe loop study of corrosion and scale formation of iron pipes, low-alkalinity waters were found to produce thick, nodular, gelatinous scales that were loosely bound to the pipe surface. Gentle scraping readily removed this scale suggesting that increased distribution flows could readily do the same. In contrast, high-carbonate waters yielded thin, hard, tightly bound scale that could not be easily scraped from the pipe surface. The influence of increased distribution flows on this type of scale would be less than on the former, resulting in less likelihood of releasing inorganic contaminants to the bulk water through changes in hydraulics.

Particulates, e.g., chemical precipitates that settle onto the surface of metallic scales, may be more easily dislodged than the scale itself. Similarly, re-suspension of accumulated sediments is likely dependent on particle size and the nature of the material itself (e.g., whether it is a chemical precipitate or a combination of organic and inorganic material).

Biofilms can be removed from the pipe surface by the erosive action of flowing water. McMath et al. (1997) conducted flow studies using both biofilm and settled bacteria. The experiments consisted of a series of flow increases to determine the effect on the numbers and nature of particles in water. A sustained peak of clumped bacteria was seen for all the flow changes indicating that biofilm was being eroded from the pipe walls even after several increases in flow. A ten-fold increase in flow resulted in up to 60% of the bacteria in the water phase being present in microcolonies or clumps. Based on the 4-inch (100-mm) pipe diameter, the flow rates tested correspond to flow velocities of 0.0033 fps (0.001 m/s) and 0.037 fps (0.01 m/s), respectively.

Biofilm resistance to increased flow also varies. Depth of film may be a significant factor. Shear forces generated by the increased flows may tend to have more influence on the thicker films.

The location of scales and biofilms will also likely impact dislocation of these accumulations of inorganic contaminants. Accumulations in crevices are less likely to be impacted by increased flows than those located on pipe surfaces. Also, those not directly in the flow path, e.g., on fixture surfaces may be less likely to be dislodged. Friedman et al. (2003) demonstrated that as the degree of tuberculation increases, the effectiveness of a flush becomes less sensitive to flushing velocity.

Flow Reversal

In arterial-loop or grid configuration distribution systems, many of the mains are interconnected so that water can flow in different directions. While this is beneficial in terms of minimizing dead-ends and increasing flow through all areas of the distribution system, on/off cycles of well pumps or booster pumps can cause sudden changes in flow direction and velocity. Rapid changes in flow direction and/or velocity can result in the re-suspension of sediment and/or the scouring of biofilms, scales and tubercles from pipe walls, with a resulting impact at the customer's tap (U.S. EPA and California DHS, 1989). Rapid changes in velocity can also result in pressure transients, as described below.

Pressure Transients

Water hammer is caused by large pressure transients that occur when the velocity in a pipeline changes rapidly, e.g., by such events as stopping a pump or by water following the rapid expulsion of air from a vent or partially open valve (Martin, 2000). This rapid change causes positive and negative pressure waves that travel along the pipeline. The pressure waves will travel back and forth until the energy is dissipated by pipe friction and other dampening effects (Friedman et al., 2004). Pressure transients associated with water hammer have the potential to dislodge accumulated scales, sediments, biofilms, and their associated inorganic contaminants and can also cause damage to system components.

Construction

Construction work adjacent to active systems, e.g., adjacent to a pipeline carrying water, may involve earthwork that sets up vibrations capable of dislodging scales, sediments, and biofilms. Activities such as connection of bypass piping or service hoses required during rehabilitation or replacement of pipelines may also create conditions that dislodge scales or biofilm in the localized area.

6.2 Chemical Release of Contaminants

Contaminants that have accumulated on or within the sediment/biofilm/scale complex may be chemically released back into the bulk water by a variety of mechanisms, including desorption, dissolution and/or phase change of the reservoir, and chemical destabilization of the reservoir. As discussed below, many of the same water quality factors that influence scale formation and contaminant accumulation can also promote chemical release when the existing or equilibrium conditions are perturbed. Chemical release can occur both intermittently and potentially on a continuous basis, depending on system conditions and the prevailing release mechanisms.

Changes in Source Water Quality

The water quality within a particular area of the distribution system may change because of a change in the source water quality that feeds it. In turn, significant bulk water quality changes may affect the affinity and capacity of various reservoirs for regulated contaminants and/or the stability of the reservoirs themselves, thereby creating the potential for contaminant release.

Changes in water quality within a particular area of the distribution system can be the result of usage patterns of different sources. For example, some utilities may substitute well water for surface water during high turbidity periods. Changes in distribution system water quality can also be attributed to natural variations in the quality of the individual sources. For example, raw surface quality may vary seasonally or even on a diurnal basis. Additionally, some wells provide water of varying quality depending on the frequency or rate of use. During low use times, a well may pull from different layers of the aquifer compared to during high use times. If treatment practices are not adjusted accordingly, such variations may alter pH, chlorine demand, and other factors that encourage release of accumulated contaminants.

Changes in Treatment

Sequesterant Addition. Sequesterants, like polyphosphates, are frequently introduced into the distribution system to control discolored water that can result from iron corrosion or precipitation of iron in the source water. The sequesterant combines with dissolved material like iron, manganese, calcium, and magnesium, preventing them from precipitating out as scale or sediment (American Chemistry Council, 2004).

The addition of sequestering agents can solubilize minerals such as iron that are part of the scale. Such solubilization can weaken the structure of the scale making it more susceptible to break-away by pressure transients, increased flow or other factors described above (American Chemistry Council, 2004). Also, polyphosphate agents may increase aluminum leaching from cement-mortar lining by attacking and softening cement linings by forming strong soluble chelates with dissolved calcium and aluminum species (Snoeyink et al., 2003). The addition of sequesterant to a distribution system may also lead to the desorption or re-solubilization of previously sorbed or co-precipitated contaminants.

pH Adjustment. Many drinking water utilities implement pH adjustment practices as part of the treatment scheme to enhance the coagulation/flocculation process, reduce the corrosion of lead and copper within the distribution system, or for other reasons. It is not uncommon for finished water pH levels to vary by ± 0.5 units during normal conditions and greater variation may occur due to seasonal or even diurnal fluctuations in source water quality. The release of adsorbed trace metals from distribution system solids can occur if high pH perturbations occur. Schock (2005) noted that "A decrease of one pH unit may cause the desorption of some metal ions, or cause significant dissolution of carbonate or oxyhydroxide minerals scales on lead, copper, iron or other pipe surfaces."

Copeland and Dionysiou (2005) demonstrated the impact of bulk water pH adjustment on arsenic desorption from distribution system solids collected from six Midwestern utilities. The results confirmed that arsenic sorption onto iron and aluminum oxides and hydroxides is reversible when pH conditions are increased. The authors noted that the rate and extent of desorption is related to the magnitude of the pH perturbation from initial conditions and the initial solids arsenic concentration.

Munk and Faure (2004) developed a natural system analog to demonstrate how small pH fluctuations could impact metals mobilization from sediments containing iron and aluminum oxides and hydroxides. The researchers noted that pH fluctuations on the order of 0.2 units considerably affected the release of Zn, Cu, Ni, Mo, and Cd.

In addition to affecting sorption processes, pH fluctuations can also affect the solubility/stability of both contaminants and accumulation reservoirs.

Inhibitor Addition. The addition of orthophosphate inhibitors is also practiced to control lead and copper corrosion. In the soil environment, phosphate has been observed to affect the desorption of arsenate from oxide solids due to competition for sorption sites (Fuller et al, 1993; Peryea, 1991) (adapted from Davis et al., 2005). Using pipe rig experiments, Davis et al. (2005) studied the impacts of phosphate addition on arsenic mobilization from solids formed in ductile iron, galvanized, and copper pipes extracted from utility water systems. The pipes were initially equilibrated with a bulk water arsenic concentration of 0.010 mg/L. The introduction of 1 mg/L of phosphate following a 3-hour stagnation period resulted in arsenic leaching that exceeded the control by 1.6 to 15 times, producing arsenic levels as high as 1.5 mg/L.

Silica has also been used as a passivating agent to prevent red water episodes attributable to iron pipe corrosion (Davis et al. 2001). Rushing et al. (Undated) demonstrated that for four months following silica addition to a cast iron pipe loop, higher levels of silica resulted in greater iron particulate release from the pipe to the bulk water. By mobilizing iron scale, the levels of regulated inorganic contaminants may also increase. The study showed that after four months, the passivating role of silica was finally observed as iron release dropped below the baseline (i.e., pre-silica addition) rate.

Changes in Disinfection.

Disinfection practices can contribute to the chemical release of IOCs as described below:

1. Starting disinfection in an existing system that has not been previously disinfected can change ORP and pH within the distribution system. As previously described, changes in ORP can have a significant impact on the mineralogy and stability of corrosion scales and accumulated deposits. In Fremont, Nebraska, Reiber et al. (1997a) found that the addition of chlorine to the previously un-chlorinated groundwater affected the composition and stability of corrosion scales on residential copper tubing, resulting in a release of copper oxide particles and the arsenic sorbed to them. Starting disinfection will also lead to the death of biological organisms in the biofilm. As the biofilm decomposes, it can release sorbed substances back into the distribution system water (Flemming, 1995). Greater Vancouver Water District in British Columbia (1990) developed a pipe loop system to investigate metal leaching from copper tubing coils, using chlorinated or chloraminated waters at varying pHs. At a pH range of 6.4-6.8, the chloraminated and chlorinated loops exhibited higher leaching than the control loop containing no disinfectant residual and a comparable pH. Although most distribution systems do not operate in this pH range, this work illustrates the impact of disinfectant residual and ORP on release phenomena.

2. Changing the disinfection method to chloramination increases the amount of nitrogen in the distribution system and may lead to an increase in nitrification, i.e., the formation of nitrite and nitrate. Nitrification can cause a decrease in pH, which in turn can impact reservoir stability/solubility and sorption/co-precipitation processes, as described earlier. Also, since chlorine has a higher standard half-cell reduction potential as compared to chloramine, changing the method of disinfection can result in a change in the bulk water ORP. At similar doses and pHs, chlorine often causes more corrosion than chloramine. However, in some cases, the corrosion rate is less problematic than the type of corrosion products developed. Lytle and Schock (unpublished) investigated potential causes of high lead levels experienced by DC WASA in Washington, DC. The researchers found that a potential cause of the higher lead concentrations could be due the change in ORP that occurred when the utility switched from using a free chlorine residual to a chloramine residual, which resulted in production of more soluble lead (II), instead of lead (IV), on piping surfaces. Since lead (II) mineral ($PbCO_3$) solubility is significantly greater than that of lead (IV) mineral oxides (PbO_2), the change in disinfectant may have caused increased lead levels in DS WASA's drinking water (Lytle and Schock, unpublished).

3. Increasing or decreasing disinfectant residual to levels not typically present can change the ORP and pH within the system, producing effects as noted above. Additionally, these changes can destabilize biofilms, resulting in an increased rate of sloughing and, in turn, release of biofilm-accumulated contaminants. In addition to intentional changes in the disinfectant dose/residual at system entry-points, disinfectant residual often exhibits variation throughout the distribution system due to water age, chlorine decay and demand effects, booster chlorination, etc. This phenomenon has the potential to produce both temporal and spatial gradients in ORP and pH.

4. Periodically changing disinfectants from chloramines to free chlorine is practiced by some water utilities as a nitrification prevention and control strategy. In some states, this practice is required annually (AWWA, 2006 – in publication). As with increasing or decreasing disinfectant residual levels, this practice also changes the ORP and pH which can impact the mineralogy, sorption capacity, and selectivity of the contaminant reservoir for certain contaminants. Additionally, this practice, which is meant to "burn out" nitrifying microorganisms, can destabilize biofilms which can result in an increased rate of sloughing and, in turn, release of accumulated contaminants.

Change in Distribution System Temperatures

Changes in the distribution system water temperature may occur due to water exposed to ambient temperatures in finished water storage reservoir exposed distribution system piping. Temperature changes may impact either the solubility of contaminants or the sorptive capacity of the contaminant reservoirs.

6.3 Relative Significance of Release Mechanisms

In the context of public health protection, the central issue regarding contaminant release is the potential for consumer exposure. However, since the current regulatory framework for inorganic and radiological contaminants is based on system entry-point monitoring (with the exception of lead and copper), as discussed further in Chapter 8, there exists substantial uncertainty regarding the actual fate and transport of these contaminants within the system, and therefore, the water quality conditions at customer taps.

Since accumulation and release episodes are inherently transient, the health concern tends to shift to potential acute and sub-chronic effects. In this regard, the key exposure variables that may impact consumer health are the magnitude (i.e., concentration spike), duration, timing, and frequency of the various release pathways. In general, these are expected to be both system- and site-specific; however, based on past and ongoing research and related case studies, the industry is developing a qualitative understanding of how the various physical and chemical release mechanisms may affect these variables.

Regarding physical release mechanisms, major hydraulic and physical disturbances such as fire flows, hydrant flushing, main breaks, and construction activities, have the potential to mobilize substantial amounts of material and produce extremely high contaminant concentrations at customer taps. However, these events are usually localized, infrequent, and of short duration, all of which help to reduce the risk of exposure. Furthermore, because of the dramatic deterioration in aesthetic water quality that is often associated with these events, consumers may be able to avoid consumption during the worst-case conditions, though the potential for exposure to high levels may persist for some time afterwards (Schock, 2005). In contrast, hydraulic disturbances associated with peak seasonal or diurnal flows, flow reversals, or pressure transients may entrain surficial or loose deposits and produce only moderate increases in contaminant concentrations at customer taps. However, these would occur more frequently and affect a larger area within the system. They would also tend to occur during daytime hours, when the likelihood of consumption is greatest.

Regarding chemical release mechanisms, there are three general phenomena of concern, each of which may affect the exposure variables differently. The first phenomenon involves chemical destabilization of existing scale, leading to its physical release. This has the potential to result in a prolonged period of particulate release or, as was observed by Reiber et al. (1997), a dramatic and widespread increase in the concentration of a host of accumulated contaminants. This could be the result of substantial changes in pH and/or ORP, possibly due to the implementation or conversion of the secondary disinfectant strategy or infrequent switching between sources of substantially different quality. These events are uncommon and, since they are controlled by the utility, it may be possible to take proactive measures to reduce the potential impact (e.g., identify vulnerable pipe sections and flush or replace in advance).

The second chemical release phenomenon involves progressive contaminant desorption due to disequilibrium with the bulk water or in combination with a change in the mineralogy and sorptive properties of the scale. This may occur due to prolonged changes in bulk water quality conditions such as pH, ORP, alkalinity, or phosphate levels, which could be attributable to implementation of a new treatment strategy or seasonal source switching, particularly between groundwater and surface water supplies. The specific contaminants released and the magnitude of their concentration increase will depend on the substrate, the initial and new water quality conditions, and factors regarding desorption kinetics and mass transfer limitations of "buried" contaminants. This phenomenon has the potential to produce a relatively long exposure period (i.e., on the order of months to years) of moderate-to-high concentrations of soluble contaminants. Desorption of a specific contaminant (e.g., arsenic) may also occur if treatment is installed to remove it from the finished water; however, assuming other water quality parameters were not significantly changed, the release would not be expected to produce levels above the original bulk water concentration if the scales had already been equilibrated to that level.

The third chemical release phenomenon involves frequent adsorption/desorption cycling due to minor changes in bulk water quality. These changes may be associated with natural variations in source water quality (e.g., diurnal pH fluctuations) or changes in source blending ratios within the system. While these may occur frequently and throughout the system, the magnitude of contaminant release is expected to be small as long as the bulk water quality perturbations are small.

As noted previously, the primary contaminant reservoirs of interest (e.g., oxides involving iron, manganese, and aluminum) tend to discolor the water when released at sufficient levels. Therefore, in certain instances that involve release or scouring of solids-associated contaminants, a degree of consumer protection may be afforded because of obvious aesthetic degradation of the water which presumably, most consumers would not use. However, Schock (2005) notes that substantial concentrations of trace inorganics and radionuclides can exist in water without imparting noticeable aesthetic problems. This could be due to the release of small particles of contaminant-bearing scale at levels that are insufficient to cause significant turbidity, the progressive desorption of soluble contaminants from scale, or the dissolution of contaminant-bearing scale.

7.0 Accumulation Occurrences

This section summarizes available information related to documented inorganic accumulation occurrences. Tables 7.1, 7.2, and 7.3 summarize accumulation findings for regulated inorganic, unregulated inorganic and radiological contaminants, respectively. These tables document what concentration of the scale would be necessary to exceed the MCL. These calculations, as presented in the tables and the following text, do not consider the rate at which the contaminant is released from the scale or the dispersion that would occur between the point of scale release and the sampling point because the magnitude and duration of release into the drinking water is not understood. Therefore, higher concentrations of scale would likely be necessary to exceed the MCL. While some of these scale concentrations are likely to occur in distribution systems, others would be highly unlikely. Table 7.4 summarizes accumulation findings and MCL exceedances in those documented occurrences where bulk water was sampled. The sections following the tables provide supplemental information and detail the case studies currently known to have investigated this phenomenon.

Table 7-1. Summary of Regulated IOC Accumulation Occurrences.

Contaminant	Sample Source [A]	Contaminant Concentration [B]	Potential for MCL Exceedance [C,D]	Reference [E]
Antimony (Sb)	Scale from lead service line	100 mg/kg	60 mg of scale per liter	Schock, 2004, City “A1”
	Flush water	0.027 mg/L	n/a	Clement and Carlson, 2004
	Reservoir Sediment	48 mg/kg	125 mg sediment per liter	Scanlan, 2003
Arsenic (As)	MnO_2 solution	1 mg/kg	10 g MnO_2 per liter	Reiber et al., 1997a
	$Fe(OH)_3$ solution	80,000 mg/kg	0.13 mg $Fe(OH)_3$ per liter	Reiber et al., 1997a
	$Cu(OH)_2$ solution	180,000 mg/kg	0.0556 mg $Cu(OH)_2$ per liter	Reiber et al., 1997a
	Scale in cast iron and galvanized pipes	1,300 mg/kg	7.7 mg of scale per liter	Reiber et al., 1997a
	Scale in copper service line	2,100 mg/kg	4.8 mg of scale per liter	Reiber et al., 1997a
	MnO_2 scale	20 mg/kg	500 mg of scale per liter	Schock, 2004
	Sediment in water main	1,400 mg/kg	7.1 mg of scale per liter	Reiber et al., 1997a
	Scale from lead service line	229 mg/kg	44 mg of scale per liter	Schock, 2004, City “D”
	Flush water	0.151 mg/L	n/a	Clement and Carlson, 2004
	Reservoir Sediment	300 mg/kg	33 mg sediment per liter	Scanlan, 2003
Barium (Ba)	Scale from lead service line	88 mg/kg	22,700 mg of scale per liter	Schock, 2004, City “A1”
Beryllium (Be)	Scale from lead service line	460 mg/kg	8.7 mg of scale per liter	Schock, 2004, City “A2”
	Scale from lead service line	290 mg/kg	13.8 mg of scale per liter	Schock, 2004, City “D”
Cadmium (Cd)	Scale from lead service line	76.8 mg/kg	65.1 mg of scale per liter	Schock, 2004, City “D”
Chromium (Cr)	Scale from lead service line	65.4 mg/kg	1,529 mg of scale per liter	Schock, 2004, City “A2”
Copper (Cu)	Scale from lead service line	350 mg/kg	3,714 mg of scale per liter	Schock, 2004, City “A”
	Scale from lead service line	1,100 mg/kg	1,182 mg of scale per liter	Schock, 2004, City “B”
	Scale in cast iron and galvanized pipes	7,600 mg/kg	171 mg of scale per liter	Reiber et al., 1997a
Lead (Pb)	Scale in cast iron and galvanized pipes	6,000 mg/kg	2.5 mg of scale per liter	Reiber et al., 1997a
	Scale in copper pipes	79 mg/kg	190 mg of scale per liter	Reiber et al., 1997a
	Flush water	1.37 mg/L	n/a	Clement and Carlson, 2004
	Reservoir Sediment	830 mg/kg	18.1 mg sediment per liter	Scanlan, 2003
	Scale in copper service lines	574 – 2940 mg/kg		Fuge et al., 1992, Aberystwyth
Mercury (Hg), inorganic	Scale from lead service line	1.24 mg/kg	1,613 mg of scale per liter	Schock, 2004, City “C”
Selenium (Se)	Scale from lead service line	7.8 mg/kg	6,410 mg of scale per liter	Schock, 2004, City “D”
Thallium (Tl)	Scale from lead service line	12.7 mg/kg	157 mg of scale per liter	Schock, 2004, City “C”

[A] The contaminant reservoir material in which the contaminant accumulates.

[B] The concentration of the contaminant in the sample (i.e., contaminant reservoir material).

[C] The amount of the source material that would need to contaminate the distribution system water in order for there to be a MCL violation of the contaminant.

[D] Action limit for lead and copper.

[E] See Section 7.3 for description of Shock, 2004.

Table 7-2. Summary of Unregulated IOC Accumulation Occurrences.

Contaminant	Sample Source[A]	Contaminant Concentration[B]	Potential for SMCL Exceedance, or Adverse Aesthetic Effect (where applicable)[C]	Reference[D]
Aluminum (Al)[E]	Scale from lead service line	121,000 mg/kg	0.41-1.65 mg of scale per liter	Schock, 2004, City “A2”
	Scale from lead service line	36,000 mg/kg	1.4-5.6 mg of scale per liter	Schock, 2004, City “A1”
	Scale from lead service line	35,900 mg/kg	1.4-5.6 mg of scale per liter	Schock, 2004, City “C”
	Leached from scale in transmission line	0.050 mg/L	n/a	Fuge et al., 1992, Llanbrynmair
	Scale in copper service lines	68 – 200 mg/kg	1,000-2,941 mg of scale per liter	Fuge et al., 1992, Aberystwyth
	Leached from scale in copper service line	0.059 mg/L	n/a	Fuge et al., 1992, Aberystwyth
Nickel (Ni)[F]	Scale from lead service line	164 mg/kg	610 mg of scale per liter	Schock, 2004, City “A2”
Silver (Ag)	Scale from lead service line	1.3 mg/kg	76,900 mg of scale per liter	Schock, 2004, City “A1”
Vanadium (V)	Scale from lead service line	182 mg/kg	n/a	Schock, 2004, City “C”
Zinc (Zn)	Scale from lead service line	36,900 mg/kg	135.5 mg of scale per liter	Schock, 2004, City “C”
	Reservoir Sediment	13,000 mg/kg	385 mg sediment per liter	Scanlan, 2003
	Leached from scale in copper service line	52 – 6510 mg/kg	25 – 125 mg/L	Fuge et al., 1992, Aberystwyth
Rare Earth Elements (REE)	Scale from lead service line	4,478 mg/kg (4,450 mg/kg Dy)	n/a	Schock, 2004, City “D”
	Scale from lead service line	794 mg/kg (646 mg/kg Dy)	n/a	Schock, 2004, City “A2”

[A] The contaminant reservoir material in which the contaminant accumulates.

[B] The concentration of the contaminant in the sample (i.e., contaminant reservoir material).

[C] The amount of the source material that would need to contaminate the distribution system water in order for there to be a MCL violation of the contaminant.

[D] See Section 7.3 for description of Shock, 2004.

[E] SMCL range of 0.05-0.2 mg/L.

[F] The MCL and MCLG were remanded on 2/9/95. EPA is reconsidering the MCL. USEPA, 1995b.

Table 7-3. Summary of Regulated Radiological Contaminant Accumulation Occurrences.

Contaminant	Sample Source[A]	Contaminant Concentration[B]	Potential for MCL Exceedance[C]	Reference[D]
Alpha Emitters	5 minute hydrant flush	57.1 pCi/L	-	Clement and Carlson, 2004, Hydrant 1.
	5 minute hydrant flush	48.2 pCi/L	-	Clement and Carlson, 2004, Hydrant 2.
Beta and Photon Emitters	10 minute hydrant flush	63.1 pCi/L	-	Clement and Carlson, 2004, Hydrant 1.
	5 minute hydrant flush	49.4 pCi/L	-	Clement and Carlson, 2004, Hydrant 2.
	Distribution System Scale	54 pCi/L of 228Ac 23 pCi/L 208Ac	-	Field et al., 1995
Radium-226/228 (226Ra/228Ra), Combined	Sorptive capacity on iron hydroxides	20 to 650 pCi/g	7.7-250 mg of scale per liter	Valentine and Stearns, 1994
	Sorptive capacity on manganese oxides	20,000 to 40,000 pCi/g	0.125-0.25 mg of scale per liter	Valentine and Stearns, 1994
	5 minute hydrant flush	12.2 pCi/L 226Ra, 5.7 pCi/L 228Ra	-	Clement and Carlson, 2004, Hydrant 1.
	5 minute hydrant flush	15.8 pCi/L 226Ra, 11.8 pCi/L 228Ra	-	Clement and Carlson, 2004, Hydrant 2.
	Scale in distribution system pipe	34.7-97.6 pCi/g 226Ra, 0.73 pCi/g 228Ra	0.05 - 0.14 g scale per liter	Aksoy et al., 2002
	Scale in distribution system pipe	270 pCi/g 226Ra	18.5 mg scale per liter	Field et al., 1995
Radon (Rn)	n/a	n/a	n/a	n/a
Uranium (U)	Scale from lead service line	20.4 mg/kg	1470 mg of scale per liter	Schock, 2004, City "C"

[A] The contaminant reservoir material in which the contaminant accumulates.

[B] The concentration of the contaminant in the sample (i.e., contaminant reservoir material).

[C] The amount of the source material that would need to contaminate the distribution system water in order for there to be a MCL violation of the contaminant

[D] See Section 7.3 for description of Shock, 2004.

Table 7-4. Summary of Contaminant Accumulation Occurrences and Actual MCL Exceedances.

Contaminant	Contaminant Concentration in Finished Water	Sample Source	Contaminant Concentration in Bulk Water Sample	MCL	Reference
Arsenic (As)	Non-Detect	Customer taps (multiple samples and locations)	1 - 5 mg/L	0.010 mg/L	Reiber et al., 1997a
Copper (Cu)	Unknown	Customer tap	313 mg/L	1.3 mg/L[A]	Reiber et al., 1997a
Alpha Emitters	1.7 pCi/L	Customer tap	19.5 pCi/L	15 pCi/L	Clement and Carlson, 2004.
Radium-226/228 (226Ra/228Ra), Combined	Unknown	Customer tap	7.3 pCi/L	5 pCi/L	Clement and Carlson, 2004.
Radon (Rn)	432 pCi/L	Customer taps (25 sample locations)	81.1 - 2,676 pCi/L	300 pCi/L[B]	Field et al., 1995
Radon (Rn)	58 – 137 pCi/L	Customer taps (6 sample locations)	70 – 1,900 pCi/L	300 pCi/L[B]	Valentine and Stearns, 1994

[A] Action limit for copper

[B] Proposed MCL for Radon

7.1 Supplemental Accumulation Information

Radium

Radium can adsorb onto preformed hydrous iron and manganese oxides and typically follows a linear sorption model (Valentine and Stearns, 1994). The sorptive capacity of radium onto preformed iron hydroxides ranges from 20 to 650 pCi/g of iron in equilibrium with 5 pCi/L of ^{226}Ra (Valentine and Stearns, 1994). The sorptive capacity of radium onto preformed hydrous manganese oxides (HMO) ranges from 20,000 to 40,000 pCi/g of manganese in equilibrium with 5 pCi/L of ^{226}Ra (Valentine and Stearns, 1994). The authors attribute the higher affinity of radium for HMO to its higher surface area and lower point-of-zero-charge relative to iron oxides. The studies in which these sorption capacities were calculated involved the batch addition of preformed metal oxides to different test waters containing varying levels of ^{226}Ra. The authors note that the sorptive capacities would be expected to depend on the conditions under which the metal oxides are formed (which could affect surface area available) and other water quality factors. For example, co-precipitation of ^{226}Ra during metal oxide formation (e.g., during treatment) may result in higher sorptive capacities than adsorption onto pre-formed metal oxide deposits within the distribution system. Also, adhesive deposits within the distribution system may be expected to have a lower available surface area than the suspended solids used in these studies.

Because radium closely resembles barium in its chemical properties, it has been found to co-precipitate with barium and strontium sulfates in scale formation (Aksoy et al., 2002).

Arsenic

Scale in cast iron and worn galvanized pipes has been found containing up to 1,300 mg/kg As (Reiber et al., 1997a). A scale concentration of 77 mg/L could cause the MCL for arsenic to be exceeded. Scale in copper pipe has been found containing up to 2,100 mg/kg As (Reiber et al., 1997a). A scale with a concentration of 4.8 mg/L could cause the MCL for arsenic to be exceeded. Up to 20 mg As/kg was found in hydrous manganese oxide scale (Schock, 2004). A scale concentration of 500 mg/L could cause the MCL for arsenic to be exceeded. An investigation found sediment in a water main containing up to 1,400 mg/kg arsenic (Reiber et al., 1997a). The MCL for arsenic could be exceeded with 7.1 mg of this sediment per liter of water. These calculations do not consider the effect of release over time or dispersion in the distribution system.

Uranium

Uranium species were found to strongly associate with the surfaces of many different iron oxide and oxyhydroxide corrosion products formed on steel surfaces (Dodge, et al. 2002). In a laboratory, six different iron oxides (ferrihydrite, goethite, green rust II, lepidocrocite, maghemite, and magnetite) were created in the presence of the uranyl ion. The results indicated that the uranium was adsorbed to the iron oxides at fractions ranging from 48,000 to 68,000 mg uranium per kilogram of iron (Dodge et al., 2002). If this material was iron scale in a distribution system, an exceedance of the uranium MCL could be accomplished by as little as 0.4

to 0.6 mg of iron per liter of water, not considering time of release and dispersion in the distribution system.

Fluoride and Cyanide

No report of accumulation of fluoride or cyanide in distribution system scale, sediment, or biofilms has been reported, so it is unknown if accumulation occurs.

Nitrate/Nitrite

No report of accumulation of nitrate or nitrite in distribution system scale, sediment, or biofilms has been found. Nitrates and nitrates are very soluble and, as such, are not expected to accumulate in the distribution system. However, under correct conditions, such as during a nitrification episode, they can form in the distribution system bulk water. Additionally, nitrification episodes can result in reduced pH and alkalinity, which in turn can increase the release of contaminants.

Radon

Radon is a noble gas and, therefore, will not chemically combine with other elements under normal conditions. Because of this, radon itself will not accumulate in the distribution system. However, radon is a daughter product from the decay of both ^{226}Ra and ^{228}Ra. Therefore an accumulation of radium will lead to higher levels of radon in the distribution system water.

7.2 Case Studies

The following case studies present data from several utilities that conducted sampling programs to assess accumulation of contaminants in the distribution system, either in response to an identified water quality problem or as part of regular maintenance activities, such as analysis of flushing materials.

Iowa, 1991, Radium and Radon

Field, et al. (1995) performed sampling and analysis to determine the cause of unnaturally high waterborne ^{222}Rn (Radon) concentrations in the Delta, Iowa municipal drinking water supply. Tap ^{222}Rn samples taken from 25 homes ranged from 81.1 to 2,676 pCi/L with a mean concentration of 1,108 pCi/L while the water entering the distribution system contained a mean concentration of 432 pCi/L of ^{222}Rn. Twenty-two of the 25 tap samples had higher concentrations than the finished water entering the distribution system. The radon source was determined to be pipe scales containing ^{226}Ra. The scale was found to contain 270 pCi/g of ^{226}Ra and 135 pCi/g of ^{222}Rn (from ^{226}Ra decay), both of which are alpha emitters. Although tap samples were not analyzed to determine whether the combined radium MCL was being exceeded, in theory a concentration greater than 18.5 mg of scale per liter of water could result in the 5 pCi/L MCL for radium being exceeded, if all the radium were released at the same time and there is no dispersion in the distribution system. Additionally, the scale was found to contain

54 pCi/g of ^{228}Ac (actinium-228)[1] and 23 pCi/g of ^{208}Tl (thallium-208)[1] both of which are beta emitters.

Iowa, 1994, Radium and Radon

Valentine and Stearns (1994) report on an investigation of radium and radon in the distribution systems of five Iowa towns. Sampling was conducted on distribution system scales, sediments, and bulk water. "Radiological "Hot Spots", defined as sampling points where radon was at least double the concentration at the point of entry to the distribution system, were found in three of the five distribution systems sampled" (Valentine and Stearns, 1994). In one system, bulk water samples from ten residential taps showed radon concentrations ranging from 70 to 1900 pCi/L. Six of the residential sample sites showed concentrations that exceeded the proposed MCL for radon of 300 pCi/L.

These high radon concentrations were attributed to scales containing radium. The ^{226}Ra content of scales sampled in one of the distribution systems ranged from 33 pCi/g in a pipe deposit to 66 pCi/g in material collected during a hydrant flush. Scale in a distribution system in another town in Iowa was sampled and the ^{226}Ra content ranged from 13 pCi/g to 32 pCi/g in a pipe deposit. Concentrations in these distribution system materials were above corresponding concentrations in the source water (i.e. accumulation had occurred).

Nebraska, 1990's, Arsenic, Copper, and Lead

Reiber et al. (1997a) reported on a case study where a colored water investigation led to findings of high levels of iron, copper, and arsenic in the distribution system. The community of Fremont, Nebraska draws its water from wells which have concentrations of iron up to 0.4 mg/L and arsenic from 0.003 to 0.008 mg/L.

After installing chlorine, caustic, and sequesterant addition at wellheads in the early to mid 1990's, intermittent colored water complaints were received with increasing frequency from homes across the distribution system. In 1996, a sample of colored water from a resident's tap yielded sediment containing more than 1000 mg/L of arsenic. It was estimated that this sediment would give the water an arsenic concentration as high as 1-10 mg/L in the bulk water. In cooperation with local homeowners, the utility collected samples of colored water under controlled conditions from several representative locations throughout the service area. The investigation determined that the colored water contained up to 412 mg/L of iron, up to 313 mg/L of copper, and from 1 to 5 mg/L of arsenic, most of which can be removed by filtration. This is 240 times the copper action limit of 1.3 mg/L, and up to 100 times the arsenic MCL of 0.010 mg/L. However, because of discoloration that would occur at these iron and copper precipitate levels, it is unlikely that customers would consume the water.

Scale in cast iron and worn galvanized pipes was found to contain up to 1.3 mg/g As, 76.3 mg/g Cu, and 6 mg/g Pb. If the scale were mobilized and released into the bulk water, temporary exceedances of drinking water standards could potentially occur. Based on these metal scale concentrations, an exceedance of the arsenic MCL and action levels for lead and copper could theoretically occur if scale were mobilized at rates of 7.9 mg/L, 17.1 mg/L, and

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[1] ^{228}Ac and ^{208}Tl are from the decay of ^{232}Th (thorium-228).

2.5 mg/L, respectively, and no dispersion or re-deposition occurred. Scale in copper pipes was found to contain up to 2.1 mg/g As, 842 mg/g Cu, and 79 mg/g Pb. Based on these metal scale concentrations, an exceedance of the arsenic MCL and action levels for lead and copper could theoretically occur if scale were mobilized at rates of 21 mg/L, 1.5 mg/L, and 0.19 mg/L, respectively, and no dispersion or re-deposition occurred. However, as discussed in Section 4.1, unless the releases are of high enough magnitude and/or of long enough duration to produce a four-quarter average that exceeds an MCL, the spikes may not result in an MCL violation

Saudi Arabia, 2002, Radium

Aksoy et al. (2002) conducted research on scales in water well discharge lines in Saudi Arabia. This research was motivated by interest and knowledge of radioactivity in scales of petroleum piping in the area and was not intended to investigate actual water quality problems. The source waters were not analyzed and the conclusions of the study focused on proper handling and disposal of the old pipes. The scale from six water well pipes in the Dammam province of Saudi Arabia was examined. The scale consisted of 89-96% iron, 2.7% calcium, up to 2.5% sulfur, 1.5 to 2.3% silicon, and up to 2% manganese. The scale contained between 34.7 and 97.6 pCi of ^{226}Ra per gram of scale and 0.73 pCi/g of ^{228}Ra. Since the U.S. NPDWS MCL for combined ^{226}Ra and ^{228}Ra is 5 pCi/L, between 0.05 and 0.14 grams of this scale per liter of water could cause the U.S. MCL to be exceeded if all the radium were released at the same time and there was no dispersion in the distribution system. The samples (crushed scales) also produced radon gas (^{222}Rn).

UK, 1992, Aluminum, Lead, and Other Heavy Metals

Fuge et al. (1992) studied the accumulation of aluminum, lead, and other heavy metals in two water distribution systems in central Wales, UK. A system in the Llanbrynmair area of Central Wales, until 1990, had obtained its water from surface sources. This source water typically had aluminum concentrations of 0.15 to 0.30 mg/L and, because of the peaty nature of the water, was clarified with aluminum sulfate. In 1990, concerned about high aluminum levels, the water company cleaned the distribution system lines and switched to a groundwater source that had an aluminum concentration of 0.001 mg/L. This study showed that elevated levels of aluminum persisted in the distribution system water, and the aluminum concentration increased with the distance traveled through the distribution system. Samples taken from domestic supplies throughout the service area revealed that after 3.1 miles, the aluminum concentration increased to 0.017 mg/L and increased to 0.050 mg/L after 11.2 miles. None of these samples exceeded the SMCL for Al. The conclusion was that aluminum was leaching from previously deposited scales.

In the Aberystwyth area of Central Wales, high lead levels were detected in the tap water of a public building during routine tests. Sampling results for the tap water were not reported. It was determined that no lead pipes were, or ever had been, used in the water supply. The building pipes were severely corroded copper pipes. Scale from these pipes, sampled at three locations within the building had lead concentrations between 574 and 2,940 mg/kg, aluminum concentrations between 68 and 200 mg/kg, and zinc concentrations between 52 and 510 mg/kg. In a test, a section of copper pipe without soldered joints was filled with domestic water, sealed, and left for 12 hours. Analysis of the water before and after the test indicated that the copper pipe increased the lead concentration from 1 to 300 µg/L, the aluminum concentration from 51 to 59 µg/L, and the zinc concentration from 25 to 125 µg/L. Laser ablation and ICP/MS analysis of the copper pipe and brass joints showed no trace of lead in the copper. The conclusion was that the scale had released the lead, aluminum, and zinc into the water.

Utah, 2000, Antimony, Arsenic, and Lead

Clement and Carlson (2004) and Scanlan (2003), report that portions of the distribution system in a Utah drinking water system were supplied by one of several sources utilized by that system, experienced significant accumulation of inorganic contaminants. The source was an abandoned silver mine (classified as groundwater). This source water had an antimony concentration of 0.0066 mg/L, most of which was in its soluble form, and arsenic and lead concentrations of 0.01016 mg/L and 0.00573 mg/L, respectively, more than half of which were insoluble particulates. The water entering the distribution system was chlorinated and had a turbidity of 0.9 ± 0.2 NTU, with no physical treatment utilized. Concentrations from samples collected during flushing were still rising after 10 minutes when sampling was discontinued: antimony at 0.027 mg/L, arsenic at 0.151 mg/L, and lead at 1.370 mg/L. This is 4, 15, and 239 times the source water concentration, respectively. It is also 4.5 times and 15.1 times greater than the antimony and arsenic MCLs, respectively, and 91 times the action limit for lead.

Scanlan (2003) also reported on sediment samples from a storage tank in the same system. The sediments, primarily iron oxides (46 wt% iron) and zinc oxides (13 wt% zinc), had average contaminant concentrations of 48 mg/kg Sb, 300 mg/kg As, and 830 mg/kg Pb. Metals accumulated in sediment and scales and were mobilized by hydraulic disturbances. Sediment concentrations of 125 mg/L, 33 mg/L, and 18 mg/L in the water could cause the antimony and arsenic MCL and lead action limit, respectively, to be exceeded. A concentration greater than 385 mg of this scale per liter of water would be required to exceed the SMCL for zinc.

Unidentified Location, Gross Alpha, Gross Beta, Radium-226 and 228

Clement and Carlson (2004) reported on a case where the source water was from two groundwater wells with a turbidity of 0.11 NTU. The distribution system transected a uranium mill tailings remedial action site. The first hydrant used for sampling was located after the piping ran through an area contaminated by the operations of a uranium mill. The second hydrant was located downstream of the contaminated area, served off a main composed of new PVC.

The system's source water had a historical average gross alpha concentration of 2.1 pCi/L, which is well below the MCL (15 pCi/L). Prior to flushing, gross alpha tap samples averaged 2.5 pCi/L, slightly higher than the source water alpha levels. After flushing was conducted across the street at Hydrant 1, a new tap sample was collected. The sample, taken 31 minutes after flushing, had a higher gross alpha concentration of 19.5 pCi/L.

Sample analysis indicated that the gross alpha concentration of the flush water peaked at 57.1 pCi/L after 5 minutes of flushing at Hydrant 1 and peaked at 48.2 pCi/L after 5 minutes of flushing at Hydrant 2. These flushed samples represent an increase of 26 times and 22 times, respectively, the historical source water concentration. Sample analysis also showed that the gross alpha concentration at one customer's tap was 19.5 pCi/L 31 minutes after Hydrant 1 was flushed. This represents an increase of 8 times the historical source water concentration, and is 1.3 times the MCL. Flushed distribution system samples at Hydrant 1 and Hydrant 2 peak concentrations (after 5 minutes of flushing) were 3.8 times and 3.2 times, respectively, higher than the MCL

Analysis also indicated that the gross beta concentration increased from 9.6 pCi/L after 30 seconds of flushing to 63.1 pCi/L after 18 minutes of flushing at Hydrant 1 and may still have been increasing. The gross beta concentration increased from non-detectable (<2.0 pCi/L) after 30 seconds of flushing to peak at 49.4 pCi/L after 2 minutes of flushing at Hydrant 2. These flushed distribution system samples show an increase in the total beta concentration of 5.6 times at Hydrant 1 and 23.7 times at Hydrant 2.

Analysis of the samples from hydrant 1 indicated the radium-226 increased from 0.6 pCi/L after 30 seconds of flushing to peak at 12.2 pCi/L after 5 minutes of flushing and the ^{228}Ra increased from non-detectable (<1.0 pCi/L) to 5.7 pCi/L. This flushed distribution system sample had a combined radium-226/228 concentration of 17.9 pCi/L which is 3.6 times the MCL. Analysis of the samples from Hydrant 2 indicated the ^{226}Ra increased from 1.1 pCi/L after 30 seconds of flushing to 15.8 pCi/L after 5 minutes of flushing and the ^{228}Ra increased from non-detectable (<1.0 pCi/L) to 11.8 pCi/L. This is a combined radium-226/228 concentration of 27.6 pCi/L which is 5.5 times the MCL.

Ultimately, it was concluded that the tailings were not the source of the emitters in the drinking water; rather, low concentrations in the source water were accumulating in the distribution system.

7.3 Case Histories Referenced by M.R. Schock (2005)

In his paper Distribution Systems as Reservoirs and Reactors for Inorganic Contaminants (2005), Schock discusses the following case histories, which included analysis of trace metal concentration in several solid materials. Table 7-5 gives the results of comprehensive chemical analysis of scale material taken from service lines in five cities. These cities are reported as anonymous distribution systems.

City "A"

City "A" is a northeastern U.S. system distributing a mix of two soft, low-alkalinity river and surface waters with 3 mg/L (as PO_4) orthophosphate addition for corrosion control. Two lead lines were evaluated.

City "A1"

The scale sample was primarily lead (50 wt%), aluminum (3.6 wt%), and manganese (3.0 wt%) but had concentrations of antimony (100 mg/kg), barium (88 mg/kg), copper (350 mg/kg), and silver (1.3 mg/kg). A concentration of 60 mg/L and 22,700 mg/L of this scale could result in an MCL exceedances for antimony and barium, respectively, if all were released at the same time and did not disperse in the distribution system.

City “A2”

The scale sample was primarily aluminum (12.1 wt%), lead (10.6 wt%), manganese (6.9 wt%), and iron (5.8 wt%) but had concentrations of beryllium (460 mg/kg), chromium (65.4 mg/kg), nickel (164 mg/kg), zinc (9,170 mg/kg), total rare earth elements (794 mg/kg), and dysprosium (646 mg/kg). A concentration of 8.7 mg/L, 1,529 mg/L and 10.7 mg/L of this scale could result in MCL exceedances for beryllium, chromium, and lead, respectively, if all were released at the same time and did not disperse in the distribution system. A concentration of 1.65 mg/L and 545 mg/L of this scale could be required to exceed the SMCL for aluminum and zinc, respectively.

City “B”

City “B” is another soft-water system in the Northeastern US that has employed different non-phosphate corrosion control approaches. The scale sample from a lead service line was primarily lead (57 wt%) but had a copper concentration of 1,100 mg/kg. A concentration greater than 1,182 mg/L of this scale could result in an action limit exceedance for copper, and a concentration greater than 38 mg/L of this scale would exceed the action limit for lead if it were all released at the same time.

City “C”

City “C” is a Midwestern utility using lime softening, with a reduced pH and zinc orthophosphate addition since the early 1980’s. The scale sample from a lead service line was primarily lead (20.6 wt%), magnesium (12.7 wt%), silicon (9.9 wt%), zinc (3.7 wt%), and aluminum (3.6 wt%), but also had mercury (1.24 mg/kg), thallium (12.7 mg/kg), uranium (20.4 mg/kg), and vanadium (182 mg/kg). A concentration of 1,613 mg/L, 157 mg/L, and 1,471 mg/L, of this scale could result in MCL exceedances for mercury, thallium, and uranium, respectively, if it were all released simultaneously. A concentration of 5.6 mg/L and 136 mg/L of this scale would be required to exceed the SMCL for aluminum and zinc, respectively.

City “D”

City “D” is a Northeastern U. S. soft surface water system. Scale material from a lead service line was primarily iron (21 wt%) and lead (≥20 wt%), but also had arsenic (229 mg/kg), beryllium (290 mg/kg), cadmium (76.8 mg/kg), selenium (7.8 mg/kg), total rare earth elements (4,478 mg/kg), and dysprosium (4,450 mg/kg). A concentration of 44 mg/L, 13.8 mg/L, 65.1 mg/L, and 6,410 mg/L, of this scale could exceed the MCLs for arsenic, beryllium, cadmium, and selenium, respectively, if it were all released at the same time.

City “E”

City “E” is a Midwestern hard ground water system with low dissolved oxygen that historically has used a polyphosphate for iron. The scale sample from an iron pipe was primarily iron (43.6 wt%). No significant concentrations of other contaminants were found on this scale.

Table 7-5. Trace Inorganic Contaminant Accumulation in Service Lines.
All units are reported as mg/kg unless shown as a percentage (i.e., weight percent).

Contaminant	City "A" Lead Pipe 1	City "A" Lead Pipe 2	City "B" Lead Pipe	City "C" Lead Pipe	City "D" Lead Pipe	City "E" Iron Pipe
Regulated IOCs						
Antimony (Sb)	100	2.54	85	5.39	27.4	0.78
Arsenic (As)	20	31.6	2	10.6	229	21.1
Barium (Ba)	88	< 0.009	1	< 0.02	< 0.009	< 0.009
Beryllium (Be)	2.1	460	<0.1	29	290	18.6
Cadmium (Cd)	7.4	16.1	0.4	0.59	76.8	0.621
Chromium (Cr)	29	65.4	< 1	4.06	6.36	14.2
Copper (Cu)	350	0.0065	1,100	0.0808	0.0896	0.195
Lead (Pb)	50%	10.6%	57%	20.6%	≥ 20%	0.0717
Mercury (Hg)	0.26	0.34	0.11	1.24	0.848	0.477
Selenium (Se)	< 1	0.3	1	0.5	7.81	< 0.2
Thallium (Tl)	0.6	0.38	0.1	12.7	0.24	< 0.06
Radiological Contaminants						
Uranium (U)	1.1	2.66	1.4	20.4	8.38	1.47
Unregulated IOCs of Potential Concern						
Aluminum (Al)	3.6%	12.1%	0.06%	3.59%	0.511%	0.0368%
Nickel (Ni)	40	164	15	68.7	21.4	8.48
Silver (Ag)	1.3	0.421	12	0.0662	0.158	0.146
Vanadium (V)	43	68.4	9	182	154	2
Zinc (Zn)	2,100	9,170	10	3.69%	687	533
Rare Earth Elements (REE)	*103*	*794*	*2*	*212*	*4,478*	*38*
Cerium (Ce)	16	8.33	0.7	3.29	2.34	0.279
Dysprosium (Dy)	3.5	646	0.093	188	4,450	35.9
Europium (Eu)	0.63	3.28	0.02	0.196	0.751	0.034
Gadolinium (Gd)	4.5	2.7	0.098	14.1	0.957	0.311
Holmium (Ho)	0.74	1.12	0.02	0.0726	0.248	0.011
Lanthanum (La)	19	38.9	0.7	1.5	5.62	0.386
Neodymium (Nd)	20	32.8	0.5	1.33	6.12	0.376
Praseodymium (Pr)	4.5	7.35	0.1	0.315	1.38	0.0901
Scandium (Sc)	0.5	2.33	< 0.5	0.28	1.1	0.18
Samarium (Sm)	4.1	6.22	0.1	0.272	1.28	0.0737
Terbium (Tb)	0.54	0.842	0.01	0.0522	0.184	0.00945
Thulium (Tm)	0.28	0.436	0.007	0.0341	0.105	0.0053
Yttrium (Y)	27	41.7	0.5	2.52	6.83	0.356
Ytterbium (Yb)	1.5	2.49	0.05	0.18	0.666	0.0323

Table 7-5. Trace Inorganic Contaminant Accumulation in Service Lines.
All units are reported as mg/kg unless shown as a percentage (i.e., weight percent).

Contaminant	City “A” Lead Pipe 1	City “A” Lead Pipe 2	City “B” Lead Pipe	City “C” Lead Pipe	City “D” Lead Pipe	City “E” Iron Pipe
Other Unregulated IOCs						
Bismuth (Bi)	340	5.97	550	1.72	2.54	0.382
Calcium (Ca)	0.2%	0.697%	<0.05%	0.756%	0.597%	0.932%
Cesium (Cs)	< 0.1	47.5	< 0.1	8.19	102	9.94
Cobalt (Co)	15	36.2	0.2	2.47	6.83	0.691
Gallium (Ga)	0.9	0.977	< 0.1	0.0633	0.275	0.00911
Germanium (Ge)	< 0.1	7.03	< 0.1	0.297	1.18	0.0674
Iron (Fe)	0.77%	5.83%	0.15%	0.356%	21.1%	43.6%
Lithium (Li)	11	34	< 0.5	< 0.6	0.8	< 0.3
Magnesium (Mg)	0.04%	0.136%	<0.01%	12.7%	0.0692%	0.0747%
Manganese (Mn)	3%	6.869%	71	781	6,240	0.031
Molybdenum (Mo)	1.3	0.465	< 0.1	8.29	6.48	13.6
Niobium (Nb)	0.1	0.905	< 0.1	0.646	0.791	0.402
Phosphorus (P)	0.74%	2.17%	< 0.01%	1.76%	0.0948%	0.0411%
Rubidium (Rb)	< 0.1	0.231	< 0.1	1.14	2.68	0.449
Silicon (Si)	NA	2.53%	NA	9.91%	2.08%	1.72%
Strontium (Sr)	14	81.6	0.4	43.7	69.4	87.7
Thorium (Th)	0.2	3.02	< 0.07	0.685	1.32	0.437
Tin (Sn)	100	1.26	210	5.47	105	5.82
Tungsten (W)	0.2	0.2	< 0.1	0.3	2.53	0.42

Source: Schock, 2004.

8.0 Regulatory Sampling and Monitoring

On January 30 1991, under the Phase II Rule, EPA promulgated the Standardized Monitoring Framework (SMF) for detecting contaminants in public drinking water supplies. The SMF was developed as MCLs were being established and monitoring requirements for specific chemicals became more and more complex. At that time, the need to provide an integrated approach for monitoring across regulated groups of contaminants (inorganic and organic contaminants, microbiological agents and radionuclides) was identified.

Overall, the intent of the SMF is to synchronize monitoring schedules for chemical and radiological contaminants across system sizes and types in order to reduce reporting variability and increase the likelihood of system compliance. The SMF applies to federal requirements for existing systems. New water systems may have different and additional requirements.

In general, the SMF requires that samples be obtained at each entry point to the distribution system. Thus, monitoring data do not necessarily reflect the water quality in the distribution system or that delivered to the consumer. This paper considers some of the implications of the point-of-entry sampling requirement.

8.1 Regulatory Monitoring for Inorganic Contaminants

With the exception of Lead and Copper Rule monitoring at selected distribution system taps, under the SMF, all community water systems (CWSs) and non-transient, non-community water systems (NTNCWSs) must monitor for all fifteen regulated inorganic contaminants (metals, arsenic, cyanide, nitrate, and nitrite) at the point(s) of entry to the distribution system. Transient, non-community water systems (TNCWSs) are only required to monitor for nitrate and nitrite. Sampling frequencies vary depending on the type of system and the contaminant concentration measured relative to the MCL for that contaminant.

8.2 Regulatory Monitoring for Radionuclides

The *Radionuclide Rule* became effective December 7, 2000 (66 FR 76708, Vol. 65, No. 236) and applies only to CWSs. The rule retains the MCLs for radium-226/228, gross alpha particles and beta particles and photon emitters that were established in 1991. The rule regulates uranium for the first time. Again, only point of entry sampling is required, except that special requirements apply for systems using sources that are contaminated by effluents from nuclear facilities.

8.3 Rationale for Standard Sampling Requirements

The SMF requirements are based on long-term (chronic) health effects risks associated with varying exposures to chemicals or radionuclides that are or may be found in water supplies. For example, if a CWS is contaminated with a small amount of a carcinogenic inorganic chemical, persons who use the water and are exposed for a long period of time may have an increased chance of getting cancer. On the other hand, persons who use water from a TNCWS (e.g., during a visit to a park) will only have a brief exposure and, therefore, a lower risk of a serious health effect. These systems are not required to monitor for chronic health risk contaminants. The MCLs for chronic contaminants are based on a running annual average, and samples may be taken up to four times a year. The SMF accounts for both natural and synthetic radiochemicals. Sampling is more intensive for the synthetic forms (beta particles and photon emitters) than the natural forms (alpha particles, radium and uranium).

Although point of entry sampling required by the SMF is effective for measuring water quality prior to the distribution system, it does not provide information on inorganic contaminant concentrations within the distribution system and in particular, transient changes in water quality such as those that can occur from inorganic contaminant accumulation and release. In some cases, such transient increases can temporarily increase the contaminant levels well above water quality standards. In other cases, it may produce levels consistently greater than the levels at the source, which may cause some systems very close to the MCL at the source to be over the MCL in the distribution system scales due to accumulation. Customer tap monitoring required by Lead and Copper Rule may provide some insight on inorganics fate and transport within the distribution system, but may not provide information on all of the inorganic parameters that can accumulate in the distribution system. The following section describes some methods that have been used to monitor contaminant accumulations and their impact on distribution water quality.

9.0 Additional Methods of Monitoring to Determine Contaminant Accumulation

Current regulatory monitoring for inorganic contaminants does not take into account that the distribution system network itself may potentially be a source of contamination. To determine the actual or potential accumulation of inorganics from scales, biofilms, and/or sediments, a different monitoring and assessment approach is needed. The following sections present some options for sampling to determine the significance of inorganic contaminant accumulations in drinking water distribution systems. The options described include the following:

- Sampling at the Tap
- Hydrant Flushing Sampling
- Examination of Scales, Sediments, and Biofilms

9.1 Sampling at the Tap

Some considerations when sampling at the tap, for the purposes of determining what levels of IOCs/rads may be accumulating within the distribution system, include sample location, sampling prior to and after flushing, sample timing, and sample procedure.

Sample Location

Typically, some of the worst quality water in the distribution system occurs at the dead ends since biofilms, sediments, and scales can accumulate in these low flow areas. If the monitoring objective is to determine contaminant accumulation it is very important to sample at low flow dead end areas.

Sampling Prior to Flushing

Sampling at the tap prior to timed hydrant flushing potentially identifies the highest contaminant levels as a result of normal chemical release or chemical re-equilibration processes from the pipeline contaminant reservoir. System hydraulic disturbances, such as flushing, could produce even more elevated concentrations of contaminants, but this is associated with physical mobilization of deposits and scales.

With regard to sampling procedure, the first-draw sampling scheme prescribed by the LCR may not be the best to use to determine release patterns and bulk water impacts within distribution system mains. Since water quality changes can occur in the mains, service connections, and home plumbing, it is recommended that separate samples are collected over time to evaluate water quality changes as water in the service line is displaced.

Sampling After Flushing

Sampling at the tap after timed hydrant flushing, or other hydraulic disturbance, involves taking a series of samples over time from the same tap that was sampled prior to initiation of hydrant flushing. This method of sampling identifies how long it takes for contaminant levels that were increased by flushing to decrease to below pre-flush levels. Typically, sampling is initiated after the water turns clear and continues until it has been demonstrated that the levels have dropped to below pre-flush levels. Clement (2004) suggests sampling the same tap after one hour, six hours, 24 hours and for as long a time period as necessary to demonstrate that contaminant levels have dropped to below pre-flush levels. By taking tap samples each month after flushing, an upwards trend may develop, indicating the need to flush again.

Sample Timing

Pressure transients or pressure waves within the distribution system are caused by changes in water velocity, or rapid changes in water demand. A system may experience the fewest pressure transients when the flow is steady for example, between midnight and 5 A.M. in the winter when people are sleeping and nighttime sprinkler use is off. By contrast morning or evening use, when people are going to or returning from work may result in the largest changes in flow patterns. It is possible that the best time to sample for the presence of IOCs in the distribution system (i.e., when the IOC concentration is routinely highest) is when a system experiences the greatest routine fluctuations in pressure. Sampling during massive hydraulic disturbances like the flows used to fight fires is not representative of the levels people would be exposed to on a routine basis. However, locations near pressure booster stations or large water users that cause large pressure transients on a routine basis might be another good location for sampling.

9.2 Hydrant Sampling

Samples collected during hydrant flushing may not be representative of water that could reach the customer’s tap. However, when considering the issue of accumulation, sampling during flushing can provide extremely valuable information on the extent of contaminant accumulation in a water system. Depending on site-specific conditions including pipe type, diameter, finished water quality, and method and time since last cleaning, hydrant flushing will remove some fraction of accumulated scale, biofilm, and sediments. Friedman et al. (2003) provides a protocol for collecting particles using hydrant nets during flushing, as well as for determining the mass of particles present in the bulk water that is flushed from the system. For particle capture with hydrant nets, the protocol requires the pipe segment be flushed *unidirectionally* with a clean water source, flushed to clear, and that at least one pipe volume be displaced through twin hydrant nets (308-micron coarse inner net and 57-micron fine outer net). For analysis of bulk water trends, sample collection after clearing the hydrant barrel includes taking samples from the water coming out of the hydrant at regular time intervals, for example, every 5 minutes. Ideally, timed samples should continue long enough to show an upwards trend, a peak and slope of the downward trend. Knowing the levels of contaminants at the peak and the time it takes to get there may be important in determining how often and how long to flush. When these timed samples are graphed it may provide valuable information for example, on unidirectional flushing leading to a steeper downward slope after the peak is reached due to the mains before it already being scoured. Sampling during high-velocity unidirectional flushing identifies contaminant accumulations that can be removed by a hydraulic disturbance and can provide a unique fingerprint of conditions in a particular system.

For example, Figure 9-1 shows the correlation between turbidity and iron concentrations measured from bulk water samples collected during several flushing exercises in one municipality. Flushing was conducted to remove iron that had accumulated within the distribution system due to years of operating a well supply with source water iron levels of approximately 0.4 mg/L. These data indicate that a flush should not be terminated until bulk water turbidity levels have been reduced to approximately 1 NTU, which, for this system, correlates to a total iron concentration that would consistently be below the 0.3 mg/L secondary MCL.

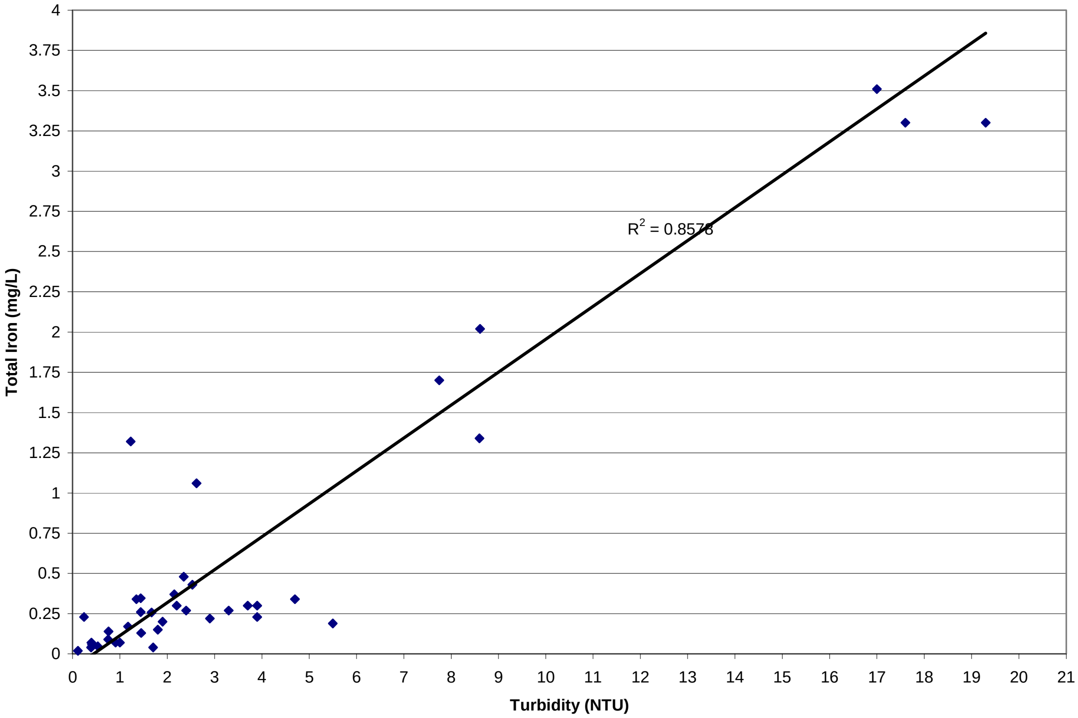

Figure 9-1. Correlation between Turbidity and Iron in Samples Collected During Hydrant Flushing

It should be noted that the location of the hydrant will make a difference in the levels of contaminants that are observed. A hydrant at a dead end has a much greater opportunity to accumulate and yield results than a hydrant located on a high velocity main. Additionally, a hydrant located downstream of cast iron piping will likely yield a larger quantity of deposits compared to a hydrant located downstream of a PVC or cement-lined portion of the distribution system.

9.3 Direct Sampling from the Pipe Interior

Direct analysis of scale, biofilm, and sediment samples will likely provide the most accurate assessment of which contaminants are accumulating in the distribution system and therefore, which potential contaminants to look for in the bulk water. Generally, there are two approaches for obtaining direct samples of the pipe interior. These include tapping the pipe and removing entire sections of the pipe from the distribution system. Most case studies involve pipe removal because replacement was already planned for those pipes and scales were readily obtained; systems were less likely to tap a good pipe just for sample collection. Because scales, biofilms and sediments can coexist as a complex, it may be difficult to isolate each fraction for collection and analysis.

Scale samples have been obtained from removed pipe sections (Aksoy et al., 2002; Field et al., 1995; Kirmeyer et al., 2000b; Reiber et al., 1997a; Schock, 2004; and Valentine and Stearns, 1994). Some researchers used scale analysis to understand the chemistry of the scales and to quantify scale compositions over their thickness. Imaging processes, such as scanning electron microscopy (SEM) and light microscopy, can provide detailed visualization of crystal structures, grain sizes, and differing lead oxidation states. Chemical properties can be identified using processes such as energy dispersive analysis, electron probe analysis, and X-ray fluorescence. X-ray diffraction provides a mineralogical evaluation of scales, describing different oxidative states of materials present.

Investigators have used different approaches to scale analysis depending on objective of analysis and available resources. For example, Aksoy et al. (2002) used γ-spectroscopy to measure activity levels of radium-226 and radium-228. Additionally, a gas analyzer was used to measure radon gas exhalations from scale materials. Chemical elements were identified using x-ray fluorescence. Finally, gamma dose rates for the scales were measured using a survey meter with a scintillator. Kirmeyer et al. 2000b conducted a detailed analysis of pipe scales including both visual and chemical analyses. Visual and imaging analyses, including visual inspection and SEM were used to consider color, odor, hardness, and extent of pipe tuberculation. X-ray diffraction and energy dispersive spectroscopy were used to identify the elements present in scale samples.

Reiber et al., (1997a) analyzed pipe scales by removing scale from pipes, drying and powdering, then dissolving scale materials in nitric acid. Inductively-Coupled Plasmaspectrometer analysis was used to determine the metal constituents of pipe scales. Bremer & Geesey (1991) used attenuated total reflectance/Fourier transform infrared spectroscopy for analysis of MIC on copper piping. This approach, which was adapted for MIC studies, can be used to study ultra-thin films of copper that are deposited on the surface of germanium internal reflection elements by biofilms in a flow-through reactor.

10.0 Potential Control Methods for Inorganic Contaminant Accumulation and Release

This section discusses potential control methods categorized by subject areas familiar to water system purveyors: water treatment, distribution system operations, distribution system maintenance, and distribution system design and construction. Many of the practices described in this section were also discussed in Sections 4, 5, or 6, since failure to implement or control them can cause scale, biofilm, and sediment formation as well as inorganic contaminant accumulation and/or release.

Most of the practices described below are commonly employed, in some form, by many water system purveyors, for reasons other than controlling the accumulation or release of inorganic contaminants within the distribution system. Understanding how these practices affect contaminant releases, and how they can be used to control them, may provide some risk management.

10.1 Water Treatment

Some of the inorganic material that accumulates in distribution systems enters as dissolved or suspended material in the bulk water. The majority of surface water systems reduce turbidity during treatment and, therefore, the amount of inorganic contaminants entering the distribution system. However, most groundwater systems are not treated to remove turbidity and do not have to meet turbidity regulations. The characteristics of the water entering the distribution system will have a significant impact on the type and quantity of inorganic contaminants that may accumulate in the system and the rate and timing of their accumulation and release. Table 10-1 lists key water quality properties, associated water treatment parameters, and likely impacts on contaminant accumulation and/or release within the scale, sediment, or biofilm reservoirs.

Table 10-1. Water Quality Impacts on Contaminant Accumulation and Release within Distribution Systems

Water Quality Property	Key Parameters	Impact/Mechanism	Contaminant Reservoir Potentially Impacted
Corrosivity	pH, alkalinity, DIC, chloride and/or sulfate	Contaminant Accumulation/Corrosion of infrastructure Contaminant Release/Leaching from pipe materials or linings	Scales
Oxidation/Reduction Potential	Dissolved oxygen, disinfectant residual, pH	Contaminant Accumulation/Precipitation (under oxidizing conditions) Contaminant Release/Dissolution (under reducing conditions)	Scales, sediments, biofilm
Hardness	Calcium, magnesium, pH	Contaminant Accumulation/Precipitation and co-precipitation	Scales, sediments
Sequesterants	Blended or polyphosphates	Contaminant Release/Dissolution of existing scales until new protective film is established Contaminant Release/Fluctuations in pH once film is established Accumulation Avoidance/Maintain solubility of metals in source water	Scales, sediments
Poor pH stability	pH, alkalinity, calcium, magnesium	Contaminant Release/ Leaching due to pH fluctuations in aggressive, poorly buffered waters Contaminant Accumulation/Uncontrolled precipitation in moderately hard waters	Scales, sediments
Turbidity	Turbidity and sediments	Contaminant Accumulation/Adsorption to turbidity particles	Sediments
Disinfectant Residual	Free chlorine, combined chlorine, ORP	Contaminant Accumulation/Precipitation of oxidized particles Contaminant Release/Biofilm penetration and possibly from change in ORP by switching from chloramines to chlorine each year Contaminant Formation/Nitrification	Biofilm, scales, sediments

10.2 Distribution System Operations

Three issues directly related to distribution system operations and maintaining water quality (Kirmeyer et al., 2000a) are:

- Minimizing bulk water detention time,
- Maintaining positive pressure, and
- Purposefully controlling the direction and velocity of the bulk water.

Some systems attempting to manage inorganic contamination problems may be able to derive some benefit from prioritizing distribution system operating practices to better manage water age, sediment accumulation, and preservation of (consistent) water quality in general. No information specifically relating operating variables to control of inorganic contaminant accumulation and release was discovered during research for this paper. However, some links are apparent.

Flow Control

Variations in flow can affect water quality in several ways as follows: rapid changes in flow direction and/or velocity can result in the re-suspension of sediment and/or the scouring of scales and biofilms from pipe walls, which can be carried to the customer's tap (Kirmeyer et al., 2000a). Mains that do not experience routine scouring velocities tend to build up sediment and generally experience longer residence times (i.e. more time for water/pipe interaction). In fact, Friedman et al. (2003) categorize smooth or slightly tuberculated pipes with routine flow velocities between 2-4 fps as "self-cleaning".

Reservoir Turnover

In the distribution system, storage facility drain-and-fill cycles promote mixing and limit water age. As finished water ages, the opportunity for water quality deterioration increases (Kirmeyer et al., 2000a). Kirmeyer et al. (2000a) recommends that one complete turnover be accomplished every 3 to 5 days at a minimum. Since releases of inorganic contaminants can occur in response to changes in water quality, maintaining a consistent water quality may limit the frequency of releases.

Booster Disinfection

If the finished water is provided with a secondary disinfectant, the consistency of water quality may be promoted by maintaining a more uniform residual across the distribution system. This may require booster disinfection to increase the residual in locations where the residual is low. In addition to maintaining a consistent water quality, this may also assist in controlling the growth of biofilms. However, booster disinfection can change the ORP of the water, potentially resulting in release of accumulated inorganic contaminants.

Mixing and Blending

Distribution systems that receive water from two or more sources with different water chemistries typically have areas in the system that will pull water from different sources depending on water usage patterns. Isolating zones so they receive water from only one source, or mixing the different waters before entry into the distribution system, can promote consistency in water chemistry and may limit contaminant releases.

Switching from Chloramines to Chlorine

Systems using chloramines to provide a disinfectant residual may switch to chlorine for short periods to control nitrification. This practice may shock biofilms present on the pipes, resulting in sloughing and, in turn, release of inorganic contaminants contained in the biofilms. Additionally, this brief switch may result in changing oxidation states of inorganic contaminants present, affecting solubility and increasing levels present in the bulk water.

10.3 Maintenance

Distribution system maintenance is a collection of general upkeep practices and repairs necessary for the efficient operation of the system (Symons et al., 2000). It includes flushing and mechanical cleaning and these activities not only directly remove some of the accumulated contaminants, they also remove some of the contaminant reservoir capacity (e.g. scale, sediment, and biofilms).

Flushing

Unidirectional flushing is more effective than conventional flushing for removing sediment from the distribution system (Oberoi, 1994). Conventional flushing results in only partial removal of suspended sediments and can create increased customer complaints due to temporary contamination of drinking water at customer taps during and immediately after the flushing event (Friedman et al., 2002). Unidirectional flushing includes isolation of pipe segments and control of velocity in the main (up to highest attainable) and can provide a stronger scouring action than conventional flushing (Friedman et al., 2002).

Main Cleaning

Main cleaning is a rigorous method of directly removing both accumulated inorganic contaminants and the reservoirs that collect them. Pipe cleaning can remove deposits from pipe walls and may be done by pigging or scraping (Walski, 2000), or by newer methods including chemical cleaning or flow-jetting (Kirmeyer, 2000a). When subsequent re-lining is not conducted, cleaning may have detrimental effects on distribution system water quality (Kirmeyer et al., 2000a). If the cleaning process exposes base metal pipe, the tuberculation process will resume and red-water problems may occur (Walski, 2000).

Storage Facility Cleaning

Storage facility cleaning is another direct way of removing accumulated sediments from the distribution system. Tank cleaning removes deposits of calcium carbonate, sediments such as iron and manganese hydroxides or oxides, and biofilms from the tank walls (Montiel and Welte, 1995 in Kirmeyer et al, 2000a). In addition to removing this material from the storage facility and thereby removing a contaminant reservoir, storage facility cleaning also reduces the opportunity for this material to enter the distribution system.

Other Maintenance Activities

Other maintenance activities that can be employed to limit the suspension of sediments and scale materials include:

- Valve exercising protocols designed to minimize the scraping of scales from valve components when not coordinated with immediate flushing. Pre-flushing valve reconnaissance that is limited to minor turning of the valve stem to assure movement can minimize sediment release.
- Hydrant testing by fire department personnel that is planned (or tracked) and supported by monitoring and response as necessary (before customer complaints). Hydrant testing can create velocity and flow direction changes within the distribution system that are capable of suspending sediment and causing turbid or colored water episodes at customer taps.
- Response to main breaks that includes thorough release-to-service protocols and recognition that the valving required to isolate the broken main may cause flow reversals or velocity changes that suspend sediments and may cause turbid or colored water episodes at customer taps.

10.4 Distribution System Design and Construction

A well-designed and constructed distribution system promotes improved water quality in many ways including the control of inorganic contaminants. System design and construction may be considered a long-term control method for inorganic contaminant accumulation and release, and may not be applicable for systems that are not adding or replacing significant quantities of infrastructure. Design standards, policies, and engineering practices that consider water quality issues may include the following:

- Materials of construction for pipelines and storage facilities, both new and replacement that are selected to minimize scaling and sediment production, depending on existing system characteristics and needs.
- Mains that are sized based on criteria that include consideration of flow control and water age issues in the near term. Over sizing lines to support future growth leads to increased water age and low velocity problems conducive to scaling and sedimentation.
- The creation of dead ends also promotes low velocities, increased water age, and creation of the inorganic contaminant accumulation reservoirs. Where system looping is not attainable, continuous blow-off devices can reduce stagnation and the accumulation sediments.
- Standards of sanitary controls for repair and construction practices that are employed to limit the introduction of sediment (e.g. silt and sand) from the exterior environment (relative to the inside of the distribution system).

11.0 Areas for Additional Research Consideration

Further research opportunities exist to provide greater certainty of the health impacts associated with drinking water distribution systems. Some areas of exploration to better understand and control inorganic contaminant accumulation and release are:

- Developing a better understanding of which contaminants are accumulating, how they are released, and the concentrations released to the bulk water.
- Identifying conditions that promote the accumulation of contaminants in the distribution system.
- Further defining the role of biofilms in accumulating and releasing inorganic contaminants.
- Developing measures or methods of assessing whether specific reservoirs are at risk..
- Developing monitoring protocols that address which medium to sample, where the sample should be taken, when the sample should be taken, and parameters sample analysis.
- Identifying reliable methods for processing and analyzing the contaminant content of solid matrices collected from distribution systems.
- Determining the most effective procedures for controlling reservoirs or the accumulation of contaminants.
- Determining the quantity or concentration of contaminants that may reach the customer's tap, compared to the concentrations measured within the distribution system itself.
- Determining the factors that control the magnitude and duration of release of inorganic contaminants from scale, sediments, and biofilms.
- Determining the relationship between bulk water quality and pipe scale properties before and after major treatment changes, such as phosphate addition, pH adjustment, and changes in disinfection.

It should be noted that a current research project co-funded by AwwaRF and USEPA entitled *Assessment of Inorganics Accumulation in Drinking Water System Scales and Sediments* (AwwaRF 3118) is currently underway. This project is working toward developing sampling and analytical protocols for distribution system sediments and scales, and will begin to assess accumulation of inorganics in several participating utility distribution systems.

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Appendix A – Health Effects of Inorganic Contaminants

Antimony

There is no information available on the health effects of sub-chronic and chronic oral exposure to antimony in humans. However, from animal studies, sub-chronic oral exposure to antimony has been shown to decrease plasma protein and hemoglobin levels and may significantly reduce lifespan. In other animal studies, chronic oral exposure to antimony has been shown to increase serum cholesterol and decrease fasting glucose levels, and decrease lifespan (Young, 1992). The chronic LOAEL derived from rat studies is 0.35 mg/kg/day. The chronic oral reference dose for humans, which was derived by applying an uncertainty factor of 1,000, is 4×10^{-4} mg/kg/day. Assuming a 70 kg person drinking 2 L of water per day, this translates into an acceptable daily intake of 0.014 mg/L.

There is limited information available on the acute health effects of oral exposure to antimony in humans. The gastrointestinal tract is the primary target for acute exposure. Symptoms of acute exposure include gastrointestinal irritation resulting in vomiting and diarrhea (Young, 1992). According to Dunn (1928), as referenced in Young (1992), a single dose of potassium antimony tartrate (equivalent to 0.53 mg Sb/kg) produced vomiting.

Arsenic

Chronic oral exposure to arsenic above the MCL may lead to disorders of the skin, neurological system, and vascular system, as well as an increased risk of cancer of the skin, liver, bladder, and gastrointestinal tract (Opresko, 1992a). With regard to non-carcinogenic endpoints, the NOAEL derived from human studies is 0.0008 mg/kg/day and the chronic oral reference dose is 3×10^{-4} mg/kg/day. Assuming a 70 kg person drinking 2 L of water per day, this translates into an acceptable daily intake of 0.01 mg/L. Regarding carcinogenic endpoints, the USEPA has placed inorganic arsenic in weight-of-evidence group A – human carcinogen. The chronic oral exposure slope factor based on skin cancer is 1.5 $(\text{mg/kg/day})^{-1}$ (RAIS, 2005).

Acute oral exposure to arsenic may cause nausea, loss of appetite, vomiting, epigastric and abdominal pain, and diarrhea. Oral doses as low as 20-60 µg/kg/day have been reported to cause acute toxic effects in some individuals (ATSDR, 1989). Severe exposures can result in acute encephalopathy, congestive heart failure, stupor, convulsions, paralysis, coma, and death. The acute lethal dose to humans has been estimated to be about 0.6 mg/kg/day (ATSDR, 1989).

Barium

Sub-chronic and chronic oral exposure to barium primarily affects the cardiovascular system resulting in elevated blood pressure. The NOAEL derived from human studies is 0.21 mg/kg/day and the chronic oral reference dose is 0.07 mg/kg/day. Assuming a 70 kg person drinking 2 L of water per day, this translates into an acceptable daily intake of 2.45 mg/L.

Acute and sub-chronic oral exposure to barium can cause vomiting, diarrhea, decreased heart rate and elevated blood pressure. Higher doses result in cardiac irregularities, weakness, tremors, anxiety and dyspnea. The estimated fatal dose of barium carbonate is about 5 grams for a 70 kg human. The LD_{50} for barium chloride is estimated at about 1 gram for a 70 kg human, and the LD_{Lo} (lowest published lethal dose) is reported to be about 0.8 grams (Francis and Forsyth, 1995).

Beryllium

Ingested beryllium (and its compounds) undergoes limited absorption in the gastrointestinal tract, forming instead insoluble precipitates at about pH 7 that pass out of the gastrointestinal tract. EPA updated the health risk assessment of beryllium in 1998. The 1998 reassessment established a new RfD of 0.002 mg/kg/day based on the small intestinal lesions of a dog dietary study (Morgareige et al., 1996) and also considered relevant studies on the toxicity of beryllium including its developmental and reproductive toxicity. Previous epidemiologic studies have suggested that beryllium and its compounds could be human carcinogens. In a study by Berg and Burbank (1972) (as referenced by Daugherty, 1992a) that covered 15 regions of the United States, a significant correlation between cancers of the breast, bone and uterus and the concentration and detection frequency of beryllium in drinking water was identified. EPA classified beryllium in Group B2, probable human carcinogen, based on clear evidence of its carcinogenicity via inhalation or injection in several animal species.

There is no information available on the health effects of acute or sub-chronic oral exposure to beryllium in humans. Based on animal studies, acute oral LD_{50} values for beryllium range from 18 mg Be/kg as beryllium fluoride in the mouse to 200 mg Be/kg as beryllium chloride in the rat (Reeves, 1986, as referenced by Daugherty, 1992a).

Cadmium

Because the toxic effects of cadmium are a function of a critical concentration being attained in a target organ, similar effects will occur following chronic exposure to low cadmium levels or short term exposure to high concentrations. Chronic oral exposure primarily affects the kidneys, resulting in renal dysfunction. Liver, bone, and blood impacts may also occur. The chronic NOAEL for oral exposure to cadmium is 0.005 mg/kg/day in drinking water and the chronic oral reference dose for humans, which was derived by applying an uncertainty factor of 10, is 5×10^{-4} mg/kg/day (Young, 1991). Assuming a 70 kg person drinking 2 L of water per day, this translates into an acceptable daily intake of 0.018 mg/L.

Acute oral exposure of 20-30 mg/kg has caused fatalities in humans, although fatal poisoning from cadmium is generally rare. Lower amounts (unspecified) may cause gastrointestinal irritation, vomiting, abdominal pain, and diarrhea (Young, 1991).

Chromium

Chromium plays a role in glucose and cholesterol metabolism and is thus an essential element for both humans and animals. Animal studies show that Cr(VI) is generally more toxic than Cr(III), but neither is particularly toxic by the oral route (Daugherty, 1992b). Cr(III) is poorly absorbed, regardless of exposure route, whereas Cr(VI) is more readily absorbed. Humans and animals localize chromium in the lung, liver, kidney, spleen, adrenals, plasma, bone marrow, and red blood cells. Well documented dermal effects include hypersensitivity reactions and "chrome holes" of the skin. Long-term exposure can cause kidney and liver damage, and can damage circulatory and nerve tissue. In long-term studies, rats were not adversely affected by 2.4 mg/kg/day of Cr(VI) or Cr(III) administered in drinking water (potassium dichromate and chromic chloride, respectively). Based on these studies, the subchronic and chronic NOAEL for oral exposure to Cr(VI) in rats is 2.4 mg/kg/day of Cr(VI). The chronic oral reference dose for humans, which was derived by applying an uncertainty factor of 500, is 0.005 mg Cr(VI)/kg/day (Daugherty, 1992b). Assuming a 70 kg person drinking 2 L of water per day, this translates into an acceptable daily intake of 0.18 mg/L.

Regarding acute oral exposure, the estimated lowest lethal dose for humans is 71 mg/kg for chromium (oxidation state not identified) and 1-5 g for unspecified Cr(VI) compounds (Daugherty, 1992b).

Copper

Copper is an essential nutrient normally present in a variety of tissues. However, long-term exposure to 2.2-7.8 mg/L in drinking water has been shown to cause gastrointestinal disturbances and liver toxicity. Individuals with Wilson's disease are particularly susceptible to chronic toxicity from copper. In animal studies, oral doses of 40 mg/kg/day caused hematological effects and at levels greater than or equal to 100 mg/kg/day kidney and liver damage. A reference dose for elemental copper is not currently available. Based on 90-day exposure studies with rats fed copper cyanide (CuCN), the NOAEL for copper is 5 mg CuCN/kg/day. The chronic oral reference dose for humans, which was derived by applying an uncertainty factor of 1,000, is 0.005 mg CuCN/kg/day (Faust, 1992a). Assuming a 70 kg person drinking 2 L of water per day, this translates into an acceptable daily intake of 0.18 mg/L as CuCN.

Regarding acute oral exposure, copper salts ingested in gram quantities may cause gastrointestinal, hepatic and renal effects characterized by numerous symptoms including abdominal pain, vomiting, diarrhea, tachycardia, convulsions, coma and death. In one incident involving sub-chronic copper exposure (1.5 years), recurrent nausea, vomiting, and abdominal pain was observed in a family after drinking water or beverages made with water containing 7.8 mg Cu/L. In another reported incident, two children who were exposed to drinking water containing 2.2-3.4 mg Cu/L for roughly 9 months exhibited hepatosplenomegaly and increased serum transaminase and bilirubin levels.

Cyanide

Cyanides are readily absorbed through oral exposure. The central nervous system is the primary target organ. A wide range of effects such as headaches, vomiting and electrocardiogram abnormalities has been reported for occupational exposure to low concentrations (Faust, 1994). Thyroid toxicity has also been reported (Faust, 1994). Based on a two-year dietary study with rats, the sub-chronic and chronic NOAEL for oral diet exposure to free cyanide is 10.8 mg/kg/day. The chronic oral reference dose of free cyanide for humans, which was derived by applying an uncertainty factor of 500, is 0.02 mg/kg/day (Faust, 1994). Assuming a 70 kg person drinking 2 L of water per day, this translates into an acceptable daily intake of 0.7 mg/L. No suitable cancer bioassays upon which to determine carcinogenicity of cyanide were available to USEPA (Faust, 1994).

Acute exposure to cyanide at levels of 50 to 100 mg (as either potassium or sodium cyanide) results almost immediately in collapse and respiratory arrest (Faust, 1994). At much lower doses (unspecified), the earliest symptoms are weakness, headache, confusion, and occasionally nausea and vomiting.

Fluoride

Reported health effects include dental fluorosis (mottled discoloration of teeth in children generally at concentrations greater than 2 mg/L) and skeletal fluorosis at concentrations that exceed the MCL of 4 mg/L. In the United States, concentrations greater than 10 mg/L, when ingested for about 20 years, have been associated with crippling skeletal fluorosis in a few recorded case studies. The MCL was considered to provide an adequate safety factor to protect against crippling skeletal fluorosis. In setting the MCL, USEPA did not consider dental fluorosis to be an adverse health effect requiring regulation under the primary drinking water standards. A secondary MCL was developed with specific public notification requirements for fluoride at concentrations greater than 2 mg/L (NRC 2006).

Lead

Lead absorption depends on the route of exposure, age and nutritional status of individuals. Adults typically absorb 10-15% of the lead ingested; children may absorb up to 50% of the intake. Toxicity is multi-targeted, causing effects in the gastrointestinal tract, blood, cardiovascular system, nervous system, kidneys, immune system and reproductive system. Lead accumulates in the blood stream leading to the potential for chronic poisoning (Davidson, 1994).

In infants and children, there are possible adverse effects at blood levels of 15-30 μg/dL, documented effects at 40-60 μg/dL, and brain damage and death at 80-100 μg/dL. Neurotoxin effects may occur in adults at blood levels of 100-120 μg/dL. Kidney problems and high blood pressure are possible in adults at high levels, but the associated levels have not been well defined. Carcinogenicity has not been determined for humans, but has been documented in animal studies. A NOAEL was not determined because it appears that lead is a non-threshold toxicant (Davidson, 1994).

Mercury

The oxidation state and chemical form of mercury are important in determining its toxicity, with mercurous salts (monovalent mercury) being less toxic than mercuric salts (divalent mercury). The primary health effects from the ingestion of inorganic mercury (salts) at low concentrations are gastrointestinal distress and kidney damage.

Based on a study with rats, the sub-chronic and chronic LOAEL for oral exposure to inorganic mercuric chloride is 0.633 mg Hg/kg/day. The sub-chronic chronic oral reference dose of inorganic mercury was determined to be $3x10^{-4}$ mg Hg/kg/day (Young, *Undated*). Assuming a 70 kg person drinking 2 L of water per day, this translates into an acceptable daily intake of 0.01 mg/L. A NOAEL has not been determined. Carcinogenicity of mercuric chloride is considered possible by USEPA based on limited animal studies. (Young, *Undated*).

Regarding acute oral exposure to mercury, lethal doses of mercuric salts are reported to be 1-4 g. (Young, *Undated*). At lower levels, acute exposure may cause gastrointestinal disorders including pain, vomiting, diarrhea and hemorrhage, and renal failure resulting in death.

Nitrite/Nitrate

The primary toxic effects of the inorganic nitrate ion result from its reduction to nitrite by microorganisms in the upper gastrointestinal tract. The principal health effect is the interaction of nitrites (produced by the conversion of nitrate into nitrite in the gastrointestinal tract) with hemoglobin, resulting in methemoglobinemia (called blue baby syndrome in infants). Epidemiological studies have shown that blue baby syndrome can occur, especially in infants less than 2 months of age, from acute ingestion of water containing 10 mg/L of nitrate (as N) or even baby formula prepared with this water. Death can occur if not treated. Sub-chronic oral exposure to similar levels amongst school-aged children has produced similar effects. For both nitrite and nitrate, a NOEL and NOAEL of 10 mg/L (as N), respectively, have been determined based on a study of infants 0 to 3 months old (Francis, 1995 and USEPA, 1997). For nitrate, assuming a 4 kg infant drinking 0.64 L of water per day, this translates into an acceptable daily nitrate intake of 1.6 mg N/kg/day. Using the NOAEL and a modifying factor of 10, the reference dose for nitrite was calculated for a 10 kg child drinking 1 L of water per day as 0.1 mg N/kg/day. A LOAEL of 11-20 mg/L (as N) in drinking water has also been determined.

Selenium

Selenium is one of the elements needed in trace amounts in the animal and human diet. Selenium is important in the regulation of ion fluxes across membrane, stimulation of antibody synthesis, activation of glutathione peroxidase (an enzyme involved in preventing oxidative damage to cells), and several other biochemical and physiological processes (Opresko, 1993).

Signs of chronic selenium toxicity in humans include loss of hair and nails, skin lesions, tooth decay, and nervous system disorders. Based on an epidemiological study of selenosis in humans, the sub-chronic and chronic NOAEL for oral exposure to selenium is 0.015 mg/kg/day. The sub-chronic and chronic oral reference dose, which was derived by applying an uncertainty factor of 3, is 0.005 mg/kg/day (Opresko, 1993). Assuming a 70 kg person drinking 2 L of water per day, this translates into an acceptable daily intake of 0.18 mg/L.

In humans, acute oral exposures (unspecified concentrations) can result in excessive salivation, shallow breathing, diarrhea, pulmonary edema, and even death. In animals, the acute oral toxicity of selenium varies with the solubility of the chemical compound in which it occurs; the more soluble compounds such as sodium selenite and sodium selenate are more toxic than the less soluble elemental selenium, selenium sulfide and selenium disulfide (ATSDR, 1989).

Thallium

Primary targets of thallium toxicity are the nervous, integumentary (skin), and reproductive systems. Hair loss (alopecia) is the most common indicator of prolonged exposures to high concentrations of thallium. Studies show that hair loss from thallium exposure usually occurs two weeks after exposure. Chronic exposures can also result in alterations of the brain, spinal cord, and peripheral nerves (Borges and Daugherty, 1994). Based on studies using rats, the

NOAEL for chronic oral exposure to thallium is 0.202 mg/kg/day. The chronic oral reference dose for thallium, which was derived by applying an uncertainty factor of 3,000, is 6.7×10^{-5} mg/kg/day (Borges and Daugherty, 1994). Assuming a 70 kg person drinking 2 L of water per day, this translates into an acceptable daily intake of 0.002 mg/L.

Acute exposure to thallium may initially produce symptoms of gastroenteritis such as nausea, vomiting, abdominal pain, and diarrhea or constipation, which may be followed by peripheral and autonomic nervous system damage including muscle weakness, delirium, tremors, and hallucinations. The minimum lethal dose (LD_{LO}) of soluble thallium salts for an adult has been estimated to be 0.2-1.4 g (3-20 mg Tl/kg) (Borges and Daugherty, 1994).

Aluminum

No acute, sub-chronic, or chronic health effects have been shown in otherwise healthy humans. Therefore, sub-chronic and chronic reference doses and reference concentrations have not been derived for aluminum. Because of poor absorption and efficient excretion of aluminum, acute oral toxicity is observed only after relatively large doses. The LD_{50} for aluminum nitrate in rats is 261 mg Al/kg and the LD_{50} for aluminum chloride in mice is 770 mg Al/kg (Bast, 1993). However, the USEPA, in coordination with Health Canada, is in the process of evaluating new information and study protocols to adequately determine aluminum potential health hazards at the established upper SMCL range of 0.2 mg/L.

Manganese

Manganese is an essential nutrient for normal physiological functioning. However, several diseases are associated with excess intake or over-exposure to manganese. There are substantial data supporting the neurological effects of inhaled manganese; however, there are few data for the association between oral exposure to manganese and toxic effects.

Some studies have suggested chronic low- and moderate-level exposure to manganese may cause neurological impairment (USEPA, 2004f). The USEPA has developed a chronic NOAEL for oral intake of manganese of 0.14 mg/kg/d. By applying an uncertainty factor of 3 and assuming 20% of daily intake is from drinking water, the USEPA has established a lifetime Health Advisory Level of 0.3 mg/L for drinking water (USEPA, 2004f).

Acute health effects from manganese ingestion at high levels include lethargy, increased muscle tonus, tremor, and mental disturbances (USEPA, 2004f). Several case reports of oral exposure to high doses of manganese have described neurological impairment as an effect, but the quantitative and qualitative details of exposure necessary to establish direct causation are lacking. The USEPA has established a 10-day Health Advisory Level of 1 mg/L.

Nickel

There is no information available on the health effects of sub-chronic and chronic oral exposure to nickel in humans. However, animal studies using rats showed effects of weight loss and liver damage from chronic exposure to nickel. Based on these studies, the NOAEL for nickel is 5 mg/kg/d. The sub-chronic and chronic oral reference dose for humans, which was derived by applying an uncertainty factor of 300, is 0.02 mg/kg/day (Young, 1995). Assuming a 70 kg person drinking 2 L of water per day, this translates into an acceptable daily intake of 0.7 mg/L. Some evidence suggests that nickel may be an essential trace element for mammals (Young, 1995).

There are cases of acute lethality due to nickel intake in gram quantities (Young, 1995). Nausea, vomiting, abdominal pain, diarrhea, headache, cough, shortness of breath, and giddiness were reported for workers of an electroplating plant who drank water contaminated with nickel chloride and nickel sulfate (1.63 g/L) (Young, 1995).

Silver

Chronic consumption of silver may lead to argyria, an irreversible gray or blue-gray discoloration of the skin and mucous membranes (Faust, 1992b). The LOAEL for silver in humans is 0.014 mg/kg/d. The sub-chronic and chronic oral reference dose for humans, which was derived by applying an uncertainty factor of 3, is 0.005 mg/kg/day (Faust, 1992b). Assuming a 70 kg person drinking 2 L of water per day, this translates into an acceptable daily intake of 0.18 mg/L.

The primary acute health effects from the ingestion of soluble silver are corrosive damage to the gastrointestinal tract, abdominal pain, diarrhea, vomiting, shock, convulsions, and death (Faust, 1992b). The estimated fatal doses of silver nitrate are greater than 10 g.

Vanadium

Vanadium toxicity is dependent on the valence state and solubility. Pentavalent vanadium (vanadate) is considered the most toxic form. Trivalent and divalent forms are less toxic, and the elemental form is considered non-toxic (Opresko, 1991). The primary targets for sub-chronic and chronic exposures to vanadium are the digestive system, kidneys, and blood, with symptoms including intestinal cramping, and diarrhea (Opresko, 1991). Based on studies with rats, the sub-chronic and chronic NOAEL for vanadium in rats is 0.7 mg/kg/d (Opresko, 1991). The sub-chronic and chronic oral reference dose for humans, which was derived by applying an uncertainty factor of 100, is 0.007 mg/kg/day. Assuming a 70 kg person drinking 2 L of water per day, this translates into an acceptable daily intake of 0.25 mg/L.

Although there is little data for acute vanadium exposure in humans, acute exposure in animals has been shown to affect the lungs, liver, kidneys, adrenal cortex, brain, spinal cord, and bone marrow, with symptoms of diarrhea, hind limb paralysis, labored respiration and convulsions that can lead to death. High concentrations may cause irreversible damage to the kidneys. A probable lethal oral dose in humans is 5-50 mg/kg (Opresko, 1991).

Zinc

Chronic oral exposure to zinc may result in anemia (Opresko, 1992b). Based on clinical data, the sub-chronic and chronic LOAEL of metallic zinc is 2.14 mg/kg/day in humans. The sub-chronic and chronic oral reference dose, which was derived by applying an uncertainty factor of 10, is 0.2 mg/kg/day (Opresko 1992b). Assuming a 70 kg person drinking 2 L of water per day, this translates into an acceptable daily intake of 7 mg/L.

Acute exposure may cause nausea, vomiting, diarrhea, and abdominal cramps. The estimated fatal dose is 40 mg/kg. Sub-chronic exposures may result in gastrointestinal upset and impairment of the immune system (Opresko, 1992b).

Rare Earth Elements

No adverse health effects for REEs have been found in the literature reviewed.

Alpha Emitters

The health effects of alpha emitters depend heavily upon how exposure takes place. External exposure (external to the body) is of far less concern than internal exposure, because alpha particles lack the energy to penetrate the outer dead layer of skin. However, if alpha emitters have been inhaled, ingested (swallowed), or absorbed into the blood stream, sensitive living tissue can be exposed to alpha radiation. The resulting biological damage increases the risk of cancer; in particular, alpha radiation is known to cause lung cancer in humans when alpha emitters are inhaled. The greatest exposures to alpha radiation for average citizens comes from the inhalation of radon and its decay products, several of which also emit potent alpha radiation (USEPA, 2004c).

Beta and Photon Emitters

Direct exposure to beta particles is a hazard because emissions from strong sources can redden or even burn the skin. However, emissions from inhaled or ingested beta particle emitters are the greatest concern. Beta particles released directly to living tissue can cause damage at the molecular level, which can disrupt cell function. Because they are much smaller and have less charge than alpha particles, beta particles generally travel further into tissues. As a result, the cellular damage is more dispersed. Some beta-emitters, such as carbon-14, distribute widely throughout the body. Others accumulate in specific organs and cause chronic exposures: Iodine-131 concentrates heavily in the thyroid gland. It increases the risk of thyroid cancer and other disorders. Strontium-90 accumulates in bone and teeth (USEPA, 2004d).

Radium

Radium-226 is a beta emitter and so has the same health effects as other alpha emitters. Radium-228 emits alpha, beta, and gamma radiation and so has the same health effects as other alpha, beta, and gamma emitters.

Radon

Radon is an alpha emitter, and so has the same health effects as other alpha emitters. Specifically, exposure to radon in drinking water increases the risk of developing cancer, particularly lung and stomach cancer (USEPA, 1999a).

Uranium

Uranium-238, -235, and -234 are all alpha emitters, and so have the same health effects as other alpha emitters. In addition to being weakly radioactive, uranium is a toxic metal. The greatest health risk from large intakes of uranium is toxic damage to the kidneys. Uranium exposure also increases the risk of cancer due to its radioactivity. Uranium tends to concentrate in specific locations in the body, increasing the risk of bone cancer, liver cancer, and blood diseases (such as leukemia) (USEPA, 2004b).